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Investigation into the effects of magnetic agitation and pulsed current on the development of Sn-Cu alloy electrodeposits

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ABSTRACT

Sn-Cu alloy electrodeposits have found a wide range of applications in the electronics, automotive and aerospace industries. In the current research, the electrodeposition of Sn-Cu alloy coatings produced from an electrolyte based on fluoroboric acids was thoroughly studied. The cathode current density was found to have a significant impact on the appearance and the surface morphology of Sn-Cu alloy electrodeposits. Our experimental results suggested that deposition current density, magnetic agitation and pulsed current parameters (pulse frequency and duty cycle) were all found to be crucial factors significantly affecting the chemical composition of the Sn-Cu alloy electrodeposits. In addition, the employment of pulsed current techniques significantly improved the edge effect and the surface roughness. Whisker growth on the Sn-Cu alloy electrodeposits was assessed. All the samples subjected to different electroplating condition were prone to develop Sn whiskers after a few weeks of storage at room temperature.

KEYWORDS

Tin-copper alloy; Electrodeposition; Thin films; Pulsed current; Tin whiskers

1. INTRODUCTION

Tin is an important metal in the industry as it can be alloyed with various metals (e.g. copper, lead, bismuth, cadmium, cobalt, nickel, and zinc) to form binary alloy systems. Tin-copper (Sn-Cu) alloys of various compositions are of high interest due to their relatively low cost and excellent corrosion resistance and have found a range of applications in sectors such as electronics, automotive and aerospace depending on their mechanical, thermal and electrical properties [1]. Electrodeposition is a comparatively inexpensive technique that is accepted as a preferred method for production of Sn-Cu alloys [2]. However, the large difference between the standard reduction potentials of Sn^{2+} (- 0.14 V versus SHE) and Cu^{2+} (+ 0.34 V versus SHE) is a major problem for electrodeposition of Sn-Cu alloys [2]. Copper ions are usually complexed by cyanide to bring the reduction potential of Sn^{2+} and Cu^{2+} closer together and their electrodeposition becomes possible [3]. The majority of early baths for electrodeposition of Sn-Cu alloys were alkaline cyanide-based solutions, which were capable of producing high quality electrodeposits [3]. However, the use of cyanide has been significantly restricted in recent electroplating baths, due to environmental concerns such as high toxicity and strict requirements for waste treatment.

Over the last few decades, researchers have been striving to develop environmentally-friendly non-cyanide electrolytes, which are capable of dissolving both tin and copper. Potential alternatives include sulphuric acids, methanesulfonic (MSA) acids, fluoroboric acids, phosphates and gluconates [4]. Cyanide-free electrolytes have tended to suffer from one or more drawbacks; for instance, instability of the electrolyte, poor quality of the electrodeposit, limited maximum coating thickness, narrow applicable current density range and low electroplating speed [5]. Among them, MSA based electrolytes have now become the most preferred non-cyanide baths for many industrial applications, due to properties such as high salt solubility, high conductivity and low toxicity [6]. A thorough overview of developments in the electrodeposition of Sn-Cu alloys produced from methanesulfonic acids (MSA) electrolytes can

be found in a recent review paper [4]. However, so far, a comprehensive understanding of the Sn-Cu coating characteristics produced from other electrolytes (e.g. fluoroboric acids, sulphuric acids, gluconates and phosphates) has not been conducted. This is the first paper that thoroughly studies Sn-Cu alloy electrodeposits produced from an electrolyte based on fluoroboric acids.

It should be noted that spontaneous whisker growth is one of the major concerns for electroplated Sn-Cu alloy coatings. It is widely accepted that Sn-Cu electrodeposits with the presence of Cu_6Sn_5 intermetallic compounds are prone to develop Sn whiskers, which can be highly problematic for the reliability of electrical and electronic equipment [7–10]. Sn-Cu electrodeposits have been extensively used in semiconductors, electronics and automotive industries where the growth of Sn whiskers may cause catastrophic electronic failures.

The present work was undertaken to investigate the effects of various electrodeposition parameters (current density, magnetic agitation and pulsed current parameters) on the characteristics of Sn-Cu alloy coatings; i.e. surface morphology, surface roughness, chemical composition and whisker growth. This research was aimed to provide an in-depth insight into the behaviour of Sn-Cu alloy electrodeposits produced from an electrolyte based on fluoroboric acids, in order to obtain effective control of the alloy electrodeposit properties.

2. EXPERIMENTAL

Pure copper panels (Yamamoto B-60-P05) of standard Hull Cell size (100 mm × 75 mm × 0.3 mm) were used as the cathode, which was firstly electroplated with a 2 µm nickel interlayer, followed by a 10 µm Sn-Cu alloy electrodeposit. The detailed information regarding the electrodeposition of the nickel interlayer can be found in a research article [11]. The Sn-Cu alloy electrodeposits were produced from a proprietary electrolyte containing tin fluoborate, copper fluoborate, fluoboric acid and anti-oxidisers. All the chemicals were purchased from Schloetter UK. The exact quantities of each component cannot be detailed as this is confidential information. A pure tin panel (Yamamoto B-59-P12) was used as the anode for the electrodeposition of Sn-Cu alloy coatings. Prior to electrodeposition, both the cathode and the

anode materials were washed with detergent (Decon 90), pickled in a 30 vol. % solution of hydrochloric acid (specific gravity (SG) 1.16) for 1 min to remove surface oxides, rinsed with deionised water and dried using hot air. Electrodeposition processes were carried out at various cathode current densities ranging from 0.5 to 5 A dm^{-2} for different deposition time to achieve a consistent thickness of 10 μm. All the chemicals were analytical grade and purchased from Fisher Scientific UK Ltd.

Hull Cell experiments were performed in a smart Hull Cell tank (Yamamoto B-53-SM), which is designed to let the solution overflow and circulate by use of a magnetic stirrer. The effect of cell hydrodynamics was investigated by applying various magnetic agitation rates (from 0 to 300 rpm) during the reaction. The effect of pulsed current parameters (pulse frequency and duty cycle) on the electroplating of Sn-Cu alloy coatings was also evaluated with the help of a benchtop pulse reverse rectifier (Plating Electronic GmbH pe86CB-20-5-25-S/GD).

The electrodeposition of Sn-Cu alloy coatings was studied using standard electroplating experiments to provide complementary results to Hull Cell analysis. Pure copper substrates (50 mm × 20 mm × 0.3 mm) were electrodeposited with a 2 μm nickel interlayer in a standard electrolytic cell, followed by the electrodeposition of a 10 μm Sn-Cu alloy coatings with current densities ranging from 0.5 to 5 A dm^{-2}.

Scanning electron microscope (SEM) analysis, using a Carl Zeiss (Leo) 1530 VP field emission gun scanning electron microscope (FEGSEM), was carried out to investigate the surface morphology of electroplated Sn-Cu alloy coatings and subsequent whisker growth from them. The accelerating voltage used for secondary electron imaging was 5 kV. The surface morphology was examined immediately after electrodeposition. Whisker growth, in terms of growth morphologies, dimensions and densities, was initially monitored immediately after deposition and then at weekly intervals. Energy dispersive x-ray (EDX) analysis of the chemical composition of electroplated Sn-Cu coatings was carried out using an Oxford Instruments X-Max 80 mm^2 EDX detector equipped in the FEGSEM with an accelerating voltage of 20 kV.

The surface roughness of the electroplated Sn-Cu alloy coatings was investigated using a scanning white light interferometry (SWLI) technique (Bruker NPFLEX).

3. RESULTS AND DISCUSSION

3.1 Hull Cell experiments

Hull Cell experiments were carried out to investigate the effects of deposition current density, magnetic agitation and pulsed current parameters (pulse frequency and duty cycle) on the characteristics (surface morphology, alloy composition and microstructure) of Sn-Cu alloy electrodeposits on copper substrates. All the Hull Cell samples were electrodeposited at a current of 1 A for 15 min. Based on the appearance after electroplating, Hull Cell samples were divided into four categories: bright, semi-bright, matte and white (shown in Figure 1).

SEM analysis of the Hull Cell samples (shown in Figure 2) apparently indicated that the cathode current density had a strong influence on the appearance and the surface morphology of electroplated Sn-Cu alloy coatings. The surface of the electrodeposit in the bright area subjected to low current densities (< 0.1 A dm^{-2}) was smooth with the presence of fine plate-like surface features (Figure 2 a and b). An increase in the current density to 0.25 A dm^{-2} resulted in a semi-bright appearance and a transition of the surface morphology to a pyramid-like structure (Figure 2 c and d). As the current density was further increased to 0.8 A dm^{-2}, the Hull Cell samples exhibited a matte and relatively rough surface with a large number of irregularly surface protrusions present on the electrodeposit surface (Figure 2 e and f). For a current density above 1 A dm^{-2}, the surface protrusions almost covered the entire surface and the electrodeposit became white (Figure 2 g and h).

EDX analysis of the Hull Cell samples suggested that the copper content in the Sn-Cu alloy electrodeposits was inversely proportional to deposition current density. The bright electrodeposit (Figure 2 a and b) contained a high copper content (~ 60 wt.%). This is because Cu, the more noble metal, was first electrodeposited on the cathode surface when a very low

current density was applied. An increase in the deposition current density resulted in the development of the surface protrusions present on the surface of the matte electrodeposit (Figure 2 e and f). EDX analysis indicated that these surface protrusions were predominantly composed of Sn (> 90 wt.%), which were in essence the Sn-rich grains and started to develop as the reduction potential of Sn was achieved. A further increase in the current density significantly promoted the development of the Sn-rich grains, as indicated by a marked decrease in the overall copper content in the alloy electrodeposit. The copper content was decreased to less than 3 wt.% when a current density exceeded 3 A dm^{-2}. These results suggested that deposition current density significantly affected the chemical composition of the electroplated Sn-Cu alloy coatings, and thus the surface morphology as well as the appearance of the electrodeposit.

In order to investigate the effects of magnetic agitation and pulsed current parameters on the electrodeposition of Sn-Cu alloy coatings, four groups of samples were prepared for Hull Cell analysis: I) direct current (DC) electroplating with magnetic agitation rates from 0 to 300 rpm, II) pulsed current (PC) electroplating at a frequency of 10 Hz and a duty cycle of 10% with magnetic agitation rates from 0 to 300 rpm, III) PC electroplating at a frequency of 10 Hz and different duty cycles from 10 to 90% with no agitation and IV) PC electroplating at a duty cycle of 10% and different pulse frequencies from 1 to 100 Hz with no agitation. The Hull Cell patterns for the four groups of samples are shown in Figure 3. Magnetic agitation was found to have a significant effect on the electroplating of Sn-Cu alloy coatings (Group I). An increase in the agitation rate contributed to a broader bright electrodeposit in the low current density areas. Since the bright area corresponded to a high copper concentration in the electrodeposit, it is suggested that the employment of magnetic agitation during reaction promoted the co-electrodeposition of copper and resulted in a higher copper content in the alloy coatings.

Hull Cell analysis of Group II samples suggested that an increase in agitation rate also facilitated the co-electrodeposition of copper for PC electrodeposited samples, as indicated by

the markedly broadened area of the bright electrodeposits. More importantly, at a given agitation rate, the bright area on the PC electroplated samples was significantly broader than that on the DC electroplated samples. The semi-bright area disappeared and was completely converted to bright on the PC electroplated samples. Based on these observations, it is suggested that PC electroplating was more favourable for the co-electrodeposition of copper and produced a higher copper content in the alloy electrodeposit.

The Hull Cell results obtained from Group III samples indicated that the use of a lower duty cycle increased bright electrodeposits. As the duty cycle was decreased, the bright area was broadened and the white area was significantly narrowed. The semi-bright area was reduced by decreasing the duty cycle and was only observed when the duty cycle was above 70%. It is thought that as the duty cycle was increased, the 'relaxation time' during PC electroplating was decreased. In other words, the impact of pulsed current was significantly weakened when a very high duty cycle was applied. This is the reason that the Hull Cell pattern of the PC electrodeposited samples subjected to a high duty cycle of 90% was very similar to that of the DC electroplated samples. For Hull Cell samples (Group IV) subjected to a consistent duty cycle of 10%, an increase in pulse frequency from 1 to 100 Hz resulted in a broader bright area in the low current density areas. The semi-bright area was only observed for samples subjected to a low pulse frequency of 10 Hz.

Based on the Hull Cell results, higher magnetic agitation rates, higher pulse frequencies and lower duty cycles were found to promote the co-electrodeposition of copper and result in a higher copper content in the Sn-Cu electrodeposit, particularly in the low current density areas.

3.2 Standard electroplating experiments

Hull Cell experiments were a rapid method used to qualitatively evaluate the behaviour of Sn-Cu alloy electroplating. In order to fully understand the effects of several key parameters on the electrodeposition of Sn-Cu alloy coatings, standard electroplating experiments combined with

EDX techniques have been used to provide complementary results to the Hull Cell analysis. As discussed in section 3.1, the Hull Cell results suggested that higher agitation rates, higher pulse frequencies and lower duty cycles favoured the electroplating of Sn-Cu alloy coatings and produced a higher copper content in the electrodeposit. In this case, a high magnetic agitation rate of 300 rpm, a high pulse frequency of 100 Hz and a low duty cycle of 10% were selected for further analysis. Four groups of samples subjected to different electroplating conditions were prepared for EDX analysis (shown in Figure 4): A) DC electroplating with no agitation, B) DC electroplating with an agitation rate of 300 rpm, C) PC electroplating at 100 Hz and 10% duty cycle with no agitation and D) PC electroplating at 100 Hz and 10% duty cycle with an agitation rate of 300 rpm. It was found that the copper content in the Sn-Cu alloy coatings was inversely proportional to the cathode current density for all the samples, irrespective of electroplating conditions. An increase in the current density resulted in a dramatic reduction in the copper content. This observation was in good agreement with the Hull Cell results. Figure 4a clearly showed that, in the low current density areas (0 to 2.5 A dm^{-2}), the highest copper content was observed from the PC electroplated samples with agitation (Group D), followed by Group B and C samples. DC electroplating with no agitation (Group A) produced the lowest copper content in the electrodeposit over all the current densities. Figure 4b highlighted the difference in copper content among the four groups of samples in the high current areas (2.5 to 5 A dm^{-2}). It is apparent that Group B and D samples, both of which were subjected to an agitation rate of 300 rpm during electrodeposition, exhibited a very similar copper content in the alloy coatings. DC electroplating with no agitation (Group A) still produced the least copper, even when subjected to high current densities. These results suggested that magnetic agitation during electrodeposition was the predominant factor that affected the chemical composition of the Sn-Cu alloy coatings. An increase in agitation rate produced a higher copper content in the electroplated Sn-Cu alloy coatings. The use of high current densities can cause copper ions to meet its mass transport limit during electrodeposition. The deposition rate of tin would increase

but the deposition rate of copper would be limited by the mass transport when a high current density is applied. In this case, the employment of magnetic agitation during the reaction can reduce the thickness of the cathode diffusion layer and enhance the mass transport of the electroactive species (i.e. copper and tin ions) to and from the electrode surface. In other words, the mass transport limit of Cu ions is improved, which facilitates the electrodeposition of copper ions and results in a higher copper content in the alloy coatings [12,13].

It is noteworthy that PC electroplating resulted in higher amounts of copper in the alloy electrodeposit than DC electroplating. PC electroplating provides a relaxation time (T_{off}), during which the electrode surfaces were depolarised and ions in the electrolyte were more evenly distributed due to mass transport. Similar to the effect of applying magnetic agitation, this helps to improve the mass transport of the copper ions during the reaction and increased the copper content in the alloy coatings. Another hypothesis is that the occurrence of oxygen evolution generated protons and resulted in a localised pH drop at the anodic side, which reduced the rate of oxygen evolution reactions and may limit the electrodeposition rate of Cu ions at the cathodic side. It is thought that PC electroplating can help to recover the ions at the reaction interface. In other words, protons generated at the anode were more evenly distributed during the relaxation time and thus the detrimental effects caused by a localised pH drop was minimised. This is probably one of the reasons that pulsed currents are more favourable for the co-electrodeposition of copper ions [14][15]. In the present work, immersion tests combined with EDX analysis have been undertaken to investigate the effect of pulsed current on the chemical composition of the Sn-Cu alloy coatings (shown in Figure 5). EDX analysis indicated a copper content of 1.7 wt.% for Sample I which was subjected to a DC electroplating process at a current density of 4 A dm^{-2} for 5 min with no agitation. A PC electroplating process was applied to Sample II at an average current density of 4 A dm^{-2} for 5 min with a pulse frequency of 100 Hz and a duty cycle of 10%. This produced an electroplated coating with a copper concentration of 2.0 wt.%. A duty cycle of 10% resulted in a short period of electrodeposition

time (T_{on} = 0.5 min) and a longer period of 'relaxation time' (T_{off} = 4.5 min) during PC electroplating. Sample III was firstly DC electrodeposited at a current density of 4 A dm^{-2} for 0.5 min (the same electrochemical deposition parameters as Sample I). EDX analysis showed a copper concentration of 1.5 wt.% after this short period of DC electroplating. Sample III was subsequently immersed in the same electrolyte solution for another 4.5 min (the same period as the relaxation time for Sample II) with no current passed. It was observed that the resultant amount of copper in Sample III after this further immersion was increased to 2.2 wt.%. In other words, the copper content of the Sn-Cu alloy electrodeposit was increased even when the sample was only immersed in the electrolyte with no current passed. To further understand this, Sample IV went through the same process as Sample III, except that the immersion time was significantly prolonged from 4.5 min to 24 h. EDX analysis immediately after immersion showed a marked increase in the amount of copper in the deposit to 48 wt.%. Based on these findings, it can be concluded that copper, the more noble metal, was spontaneously deposited on the Sn-Cu alloy electrodeposit by an 'immersion plating' process during the 'relaxation time', which was associated with the increased Cu content of the PC electroplated samples.

A more thorough study with regard to the mechanism for the development of Sn-Cu alloy coatings produced by PC electrodeposition can be found in a recent research article [16]. The increased copper content for PC electrodeposited samples was attributed to the occurrence of a metal displacement reaction between Sn and Cu during the 'relaxation' time. Sn-Cu coatings produced by PC electrodeposition were essentially composed of a dual layer of Sn-Cu electrodeposits and Cu_6Sn_5 intermetallic compounds (IMCs) [16].

3.3 Improvement of Sn-Cu electroplating using pulsed current techniques

3.3.1 Edge effect

The effects of magnetic agitation and pulsed current parameters on the edge effect were investigated using EDX analysis (shown in Figure 6), which suggested that DC electroplating with and without magnetic agitation demonstrated significant edge effect, as indicated by a

marked decrease by ~ 50% in copper content at the edge of the samples. With regard to the PC electrodeposited samples, the copper content at the edge was slightly lower than that in the central areas. Therefore, the employment of pulsed current techniques was capable of reducing the edge effect and resulting in a more uniform electrodeposit with a consistent chemical composition over the entire electrodeposit surface.

3.3.2 Surface roughness

Scanning white light interferometry (SWLI) has been used to investigate the surface roughness of Sn-Cu alloy coatings subjected to different electroplating conditions: A): DC electroplating with no magnetic agitation, B): DC electroplating under an agitation rate of 300 rpm, C): PC electroplating at 100 Hz and 10% with no agitation and D): PC electroplating at 100 Hz and 10% and under an agitation rate of 300 rpm. SWLI analysis of the four groups of samples is shown in Figure 7. It is apparent that samples subjected to DC electroplating (Group A and B) exhibited a relatively rough surface with an average roughness (R_a) of > 0.3 µm and a peak roughness (R_p) of > 1.8 µm. The use of magnetic agitation had little impact on the surface roughness of the Sn-Cu electrodeposit. The deposit surface became smoother when PC electroplating was introduced (Group C and D), as indicated by a decrease in both the average roughness (R_a) to ~ 0.2 µm and the peak roughness (R_p) to ~ 1.6 µm. The employment of pulsed current techniques improved the surface roughness of the electroplated Sn-Cu alloy coatings. These findings are in good agreement with previous studies that PC electroplating was capable of producing a smoother deposit surface. The authors rationalised that PC electroplating improved the mass transport of ions in the electrolyte, which promoted nuclei initiation and increased the number of nuclei on the cathode surface, resulting in finer grains and a smoother electrodeposit surface. Another hypothesis is that the occurrence of the metal displacement reaction during PC electroplating may dissolve the protrusions of tin features on the surface and thus contribute to a smoother surface [14][15].

3.4 Whisker growth analysis

In terms of the propensity of whisker growth on Sn-Cu electrodeposits on copper substrates, there is, at present, no widely accepted conclusion. Previous research has proposed that Sn-Cu alloy electrodeposit was a promising substitution for Sn-Pb, providing effective whisker mitigation [17]. However, conflicting results were reported by other researchers that Sn-Cu electrodeposits were susceptible to whisker growth, due to the formation of Sn-Cu intermetallic compounds in the alloy coatings, which produced a large residual stress within the electrodeposit and facilitated the formation and growth of Sn whiskers [7–10]. In the present study, four groups of Sn-Cu samples electrodeposited with different electroplating conditions: A): DC electroplating with no magnetic agitation, B): DC electroplating under an agitation rate of 300 rpm, C): PC electroplating at 100Hz and 10% with no agitation and D): PC electroplating at 100 Hz and 10% and under an agitation rate of 300 rpm were prepared to assess Sn whiskers growing from them. Whisker growth on these samples was monitored using FEGSEM immediately after electrodeposition and then every week. FEGSEM analysis (Figure 8) showed that a considerable number of Sn whiskers were observed on the DC electroplated samples (Group A and B) within 1 week of storage at room temperature (Figure 8a and c). Some of the large whiskers were longer than 50 µm in length (Figure 8d). In contrast, the PC electroplated samples (Group C and D) only developed a few small whiskers after 1 week of storage (Figure 8e and f). After a further 10 weeks, it was observed that all the groups of samples were populated with a high density (~ 7000 per mm^2) of large Sn whiskers, regardless of electroplating conditions (shown in Figure 9). These results suggested that the employment of PC electroplating only prolonged the incubation time for whisker formation by a few weeks, but not effectively inhibited Sn whisker growth over long timescales. The rate of Sn whisker growth on the PC and the DC electrodeposited samples significantly accelerated after a few weeks of storage at room temperature.

4. CONCLUSIONS

Hull Cell results suggested that the appearance and the surface morphology of electroplated Sn-Cu alloy coatings on copper substrates with the presence of an electroplated nickel interlayer was a function of deposition current density. In addition, high magnetic agitation rates, high pulse frequencies and low duty cycles were favourable for the co-electrodeposition of copper and resulted in a higher copper content in the alloy coatings, particularly for cathode current densities lower than 2.5 A dm^{-2}.

Standard electroplating experiments were carried out to provide complementary information to the Hull Cell results. It is suggested that copper content in the Sn-Cu alloy coatings was inversely proportional to deposition current density. Magnetic agitation during electrodeposition was the predominant factor that affected the chemical composition of the alloy coatings. An increase in agitation rate to 300 rpm produced a higher copper content in the electroplated Sn-Cu alloy coatings. PC electroplating was more favourable for the co-electrodeposition of copper, compared with DC electroplating. This is because copper ions in the electrolyte were immersion deposited on the cathode surface during the 'relaxation time' (T_{off}) of PC electroplating. Sn-Cu coatings produced by PC electrodeposition were essentially composed of a dual layer of Sn-Cu electrodeposits and Cu_6Sn_5 intermetallic compounds (IMCs).

The introduction of PC electroplating significantly improved the edge effect and the surface roughness and produced a smoother electrodeposit with a consistent chemical composition over the entire deposit surface, whilst magnetic agitation was found to have little impact on the surface roughness and the edge effect.

Whisker analysis indicated that electroplated tin-rich Sn-Cu alloy coatings on copper substrates with the presence of an electroplated nickel interlayer were prone to develop Sn whiskers. The use of PC electroplating significantly retarded whisker growth within the first few weeks of storage. However, all the samples were populated with a considerable number of large Sn whiskers after 11 weeks of storage at room temperature.

5. ACKNOWLEDGEMENTS

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LIST OF FIGURE CAPTIONS

Figure 1 Optical image showing the appearance of a Hull cell sample direct current electrodeposited at a current of 1 A for 15 min with no agitation

Figure 2 FEGSEM images showing the surface morphology and the chemical composition of Hull cell samples (direct current electrodeposited at a current of 1 A for 15 min with no agitation) in different current density areas: a) and b) bright area, c) and d) semi-bright area, e) and f) matte area and g) and h) white area

Figure 3 Hull cell patterns of Sn-Cu alloy coatings (direct current electrodeposited at a current of 1 A for 15 min) subjected to different electroplating conditions: I) DC electroplating with different agitation rates from 0 to 300 rpm, II) PC electroplating at 10 Hz and 10% with different agitation rates from 0 to 300 rpm, III) PC electroplating at 10 Hz and different duty cycles from 10 to 90% with no agitation and IV) PC electroplating at 10% and different pulse frequencies from 1 to 100 Hz with no agitation

Figure 4 a) EDX analysis showing the effects of deposition current density (from 0 to 5 A dm^{-2}), magnetic agitation (300 rpm) and pulsed current electrodeposition (100 Hz and 10% duty cycle) on the copper content in the electroplated Sn-Cu alloy coatings and b) a magnified curve showing the change of the copper content in the high current density areas from 2.5 to 5 A dm^{-2}.

Figure 5 EDX analysis showing copper content in the Sn-Cu alloy coatings subjected to different preparation conditions: I) DC electrodepositing at 4 A dm^{-2} for 5 min, II) PC electrodepositing at 4 A dm^{-2} for 5 min, III) DC electrodepositing at 4 A dm^{-2} for 0.5 min and then immersed in the same electrolyte for 4.5 min and IV) DC electrodepositing at 4 A dm^{-2} for 0.5 min and then immersed in the same electrolyte for 24 h

Figure 6 EDX analysis showing the effects of magnetic agitation (300 rpm) and pulsed current electrodeposition (100 Hz and 10% duty cycle) on the edge effect for the Sn-Cu alloy coatings electroplated at a current density of 4 A dm^{-2} for 5 min

Figure 7 SWLI analysis showing the effects of magnetic agitation and pulsed current electrodeposition on the surface roughness of the Sn-Cu alloy coatings electroplated at a current density of 4 A dm^{-2} for 5 min: a) DC electroplating with no agitation, b) DC electroplating under agitation at 300 rpm, c) PC electroplating at 100 Hz and 10% with no agitation and d) PC electroplating at 100 Hz and 10% and under agitation at 300 rpm

Figure 8 FEGSEM analysis showing whisker growth on the Sn-Cu alloy coatings electroplated at a current density of 4 A dm^{-2} for 5 min after 1 week of storage: a) and b) DC electroplating with no agitation, c) and d) DC electroplating under agitation at 300 rpm, e) PC electroplating at 10 Hz and 10% with no agitation and f) PC electroplating at 10 Hz and 10% and under agitation at 300 rpm

Figure 9 FEGSEM analysis showing whisker growth on the Sn-Cu alloy coatings electroplated at a current density of 4 A dm^{-2} for 5 min after 11 weeks of storage: a) DC electroplating with no agitation, b) DC electroplating under agitation at 300 rpm, c) PC electroplating at 10 Hz and 10% with no agitation and d) PC electroplating at 10 Hz and 10% and under agitation at 300 rpm

FIGURES

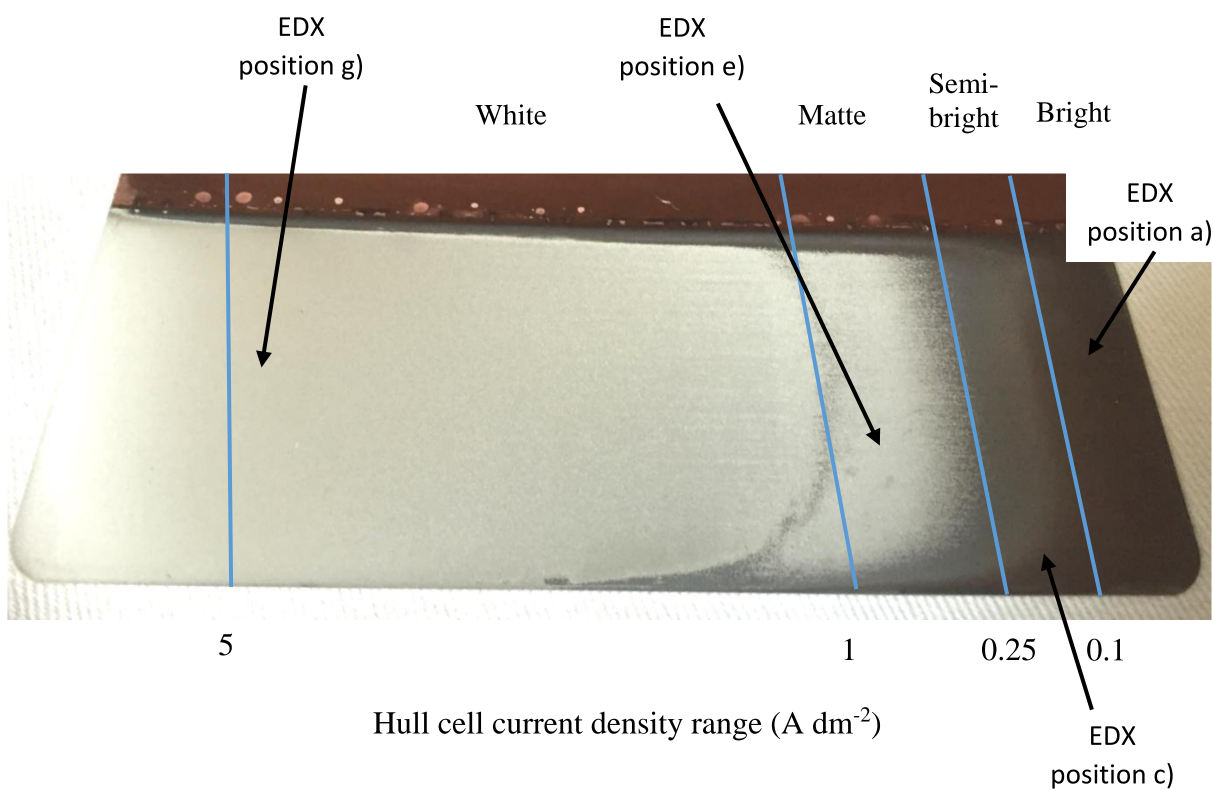
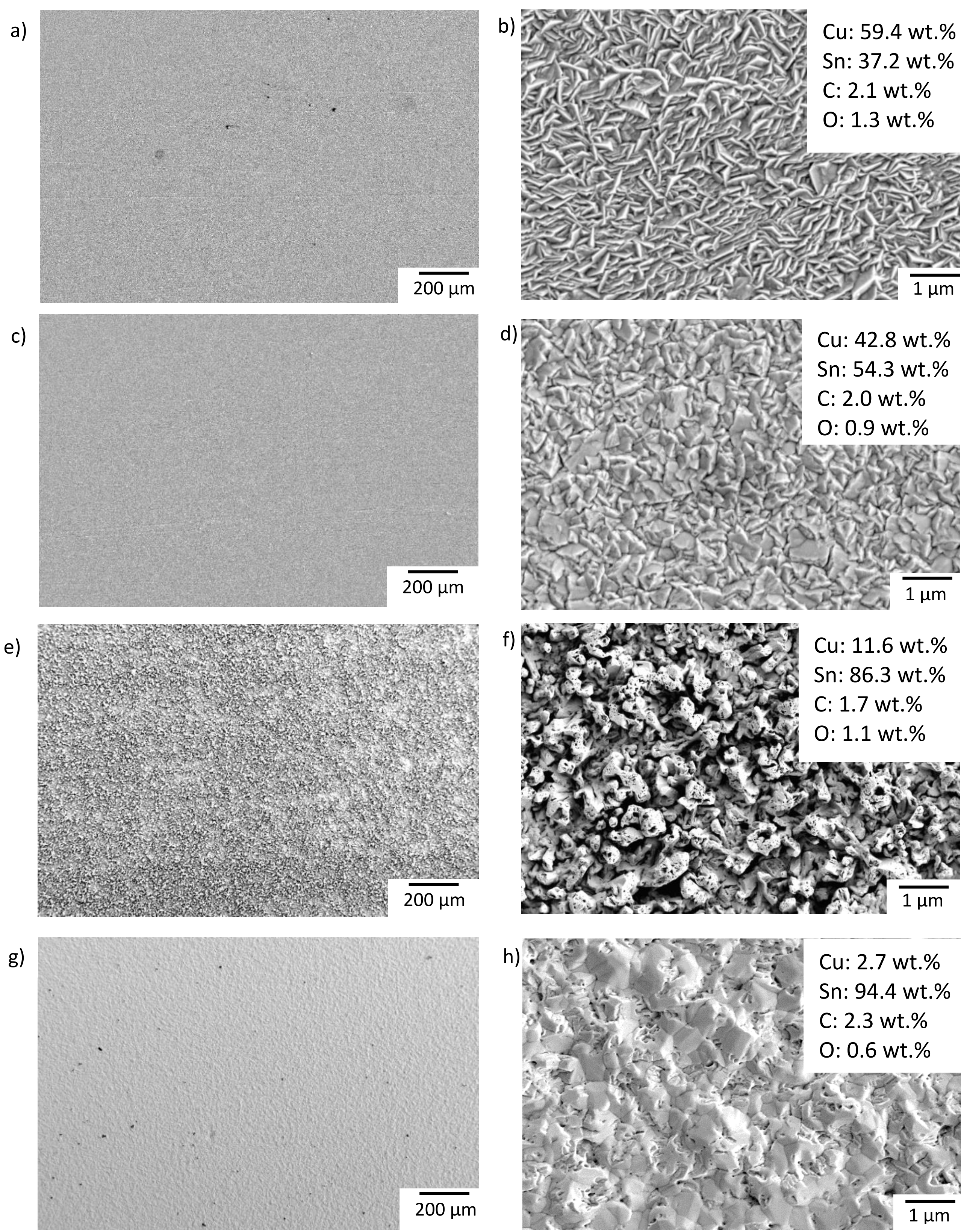


Figure 1



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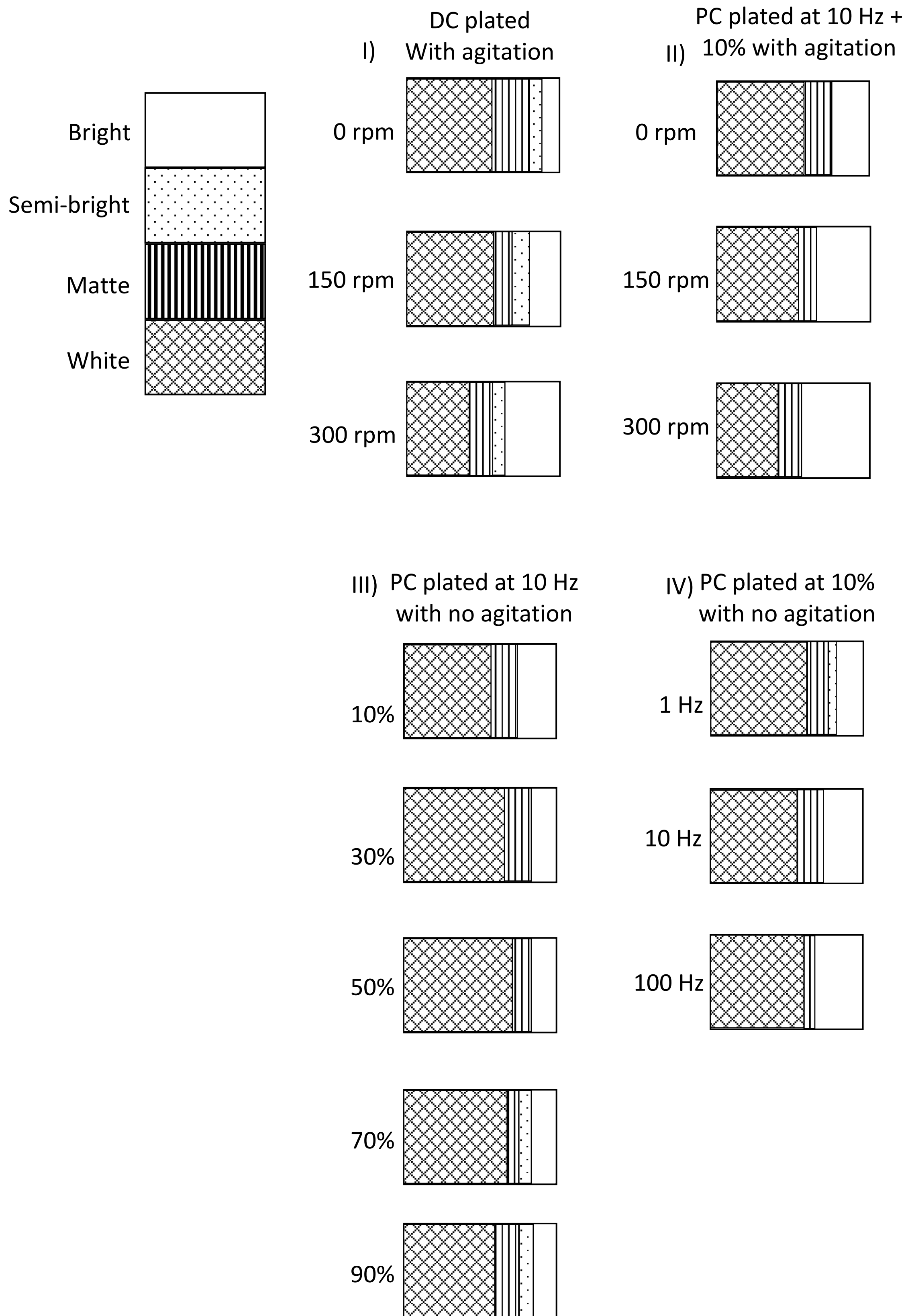

Figure 3

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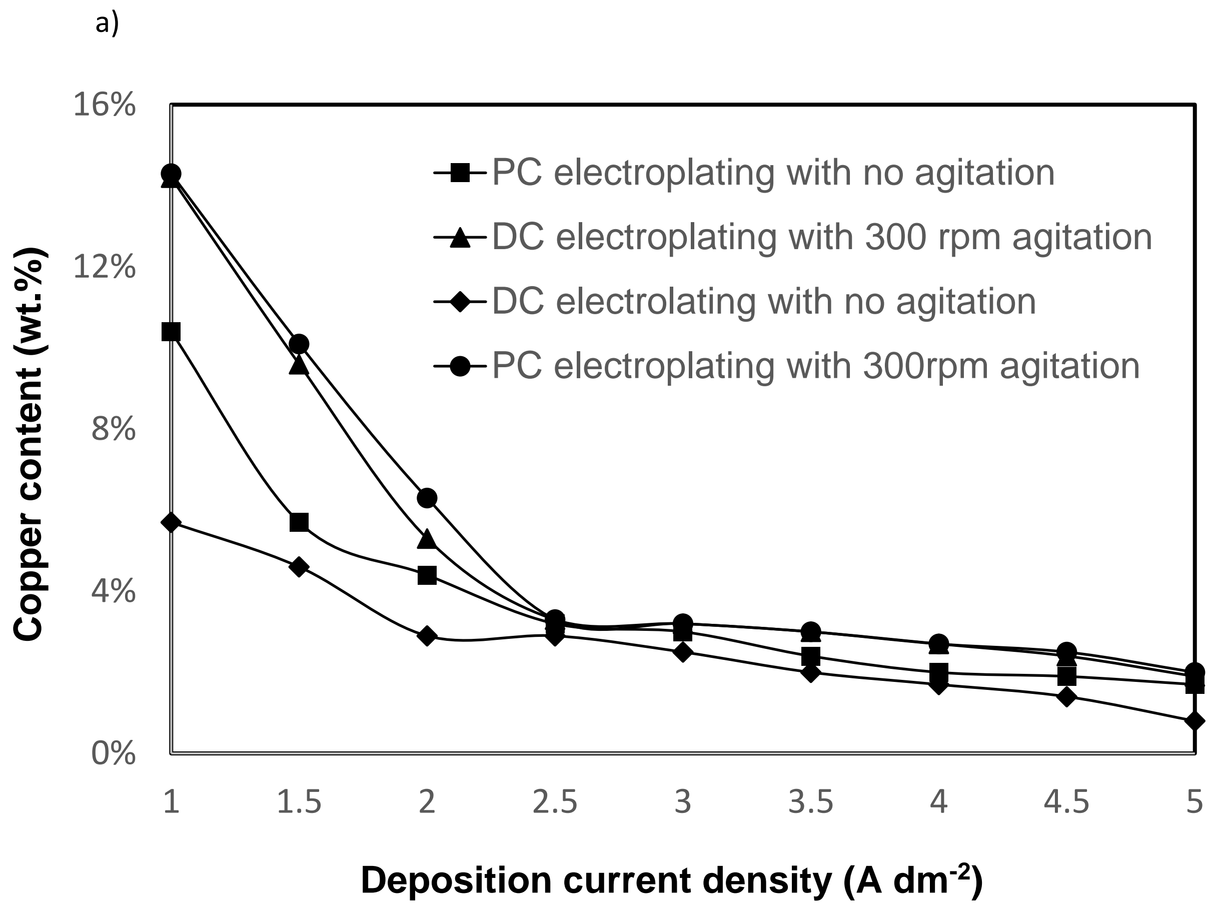

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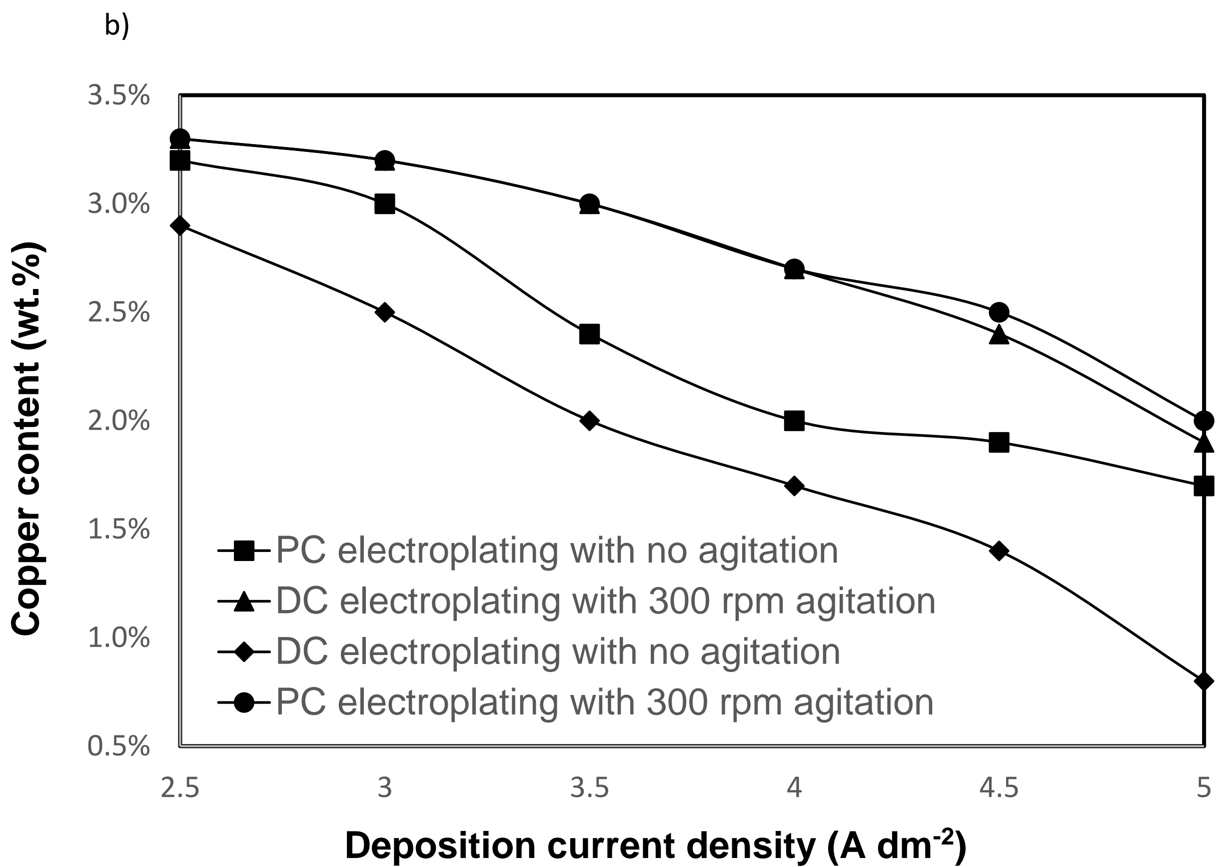

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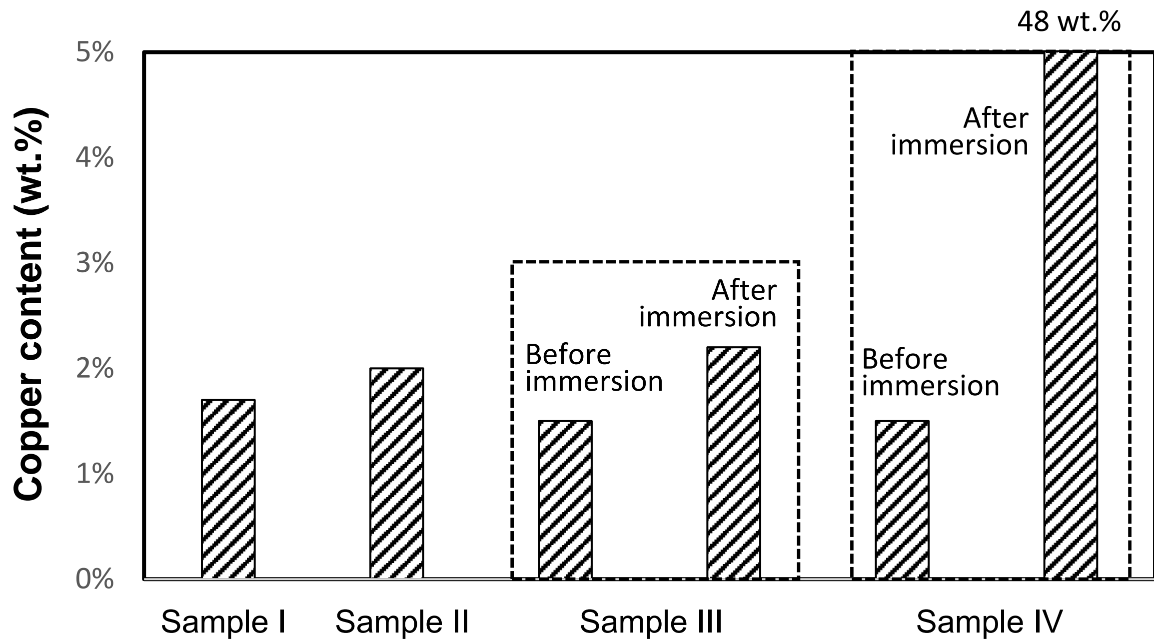

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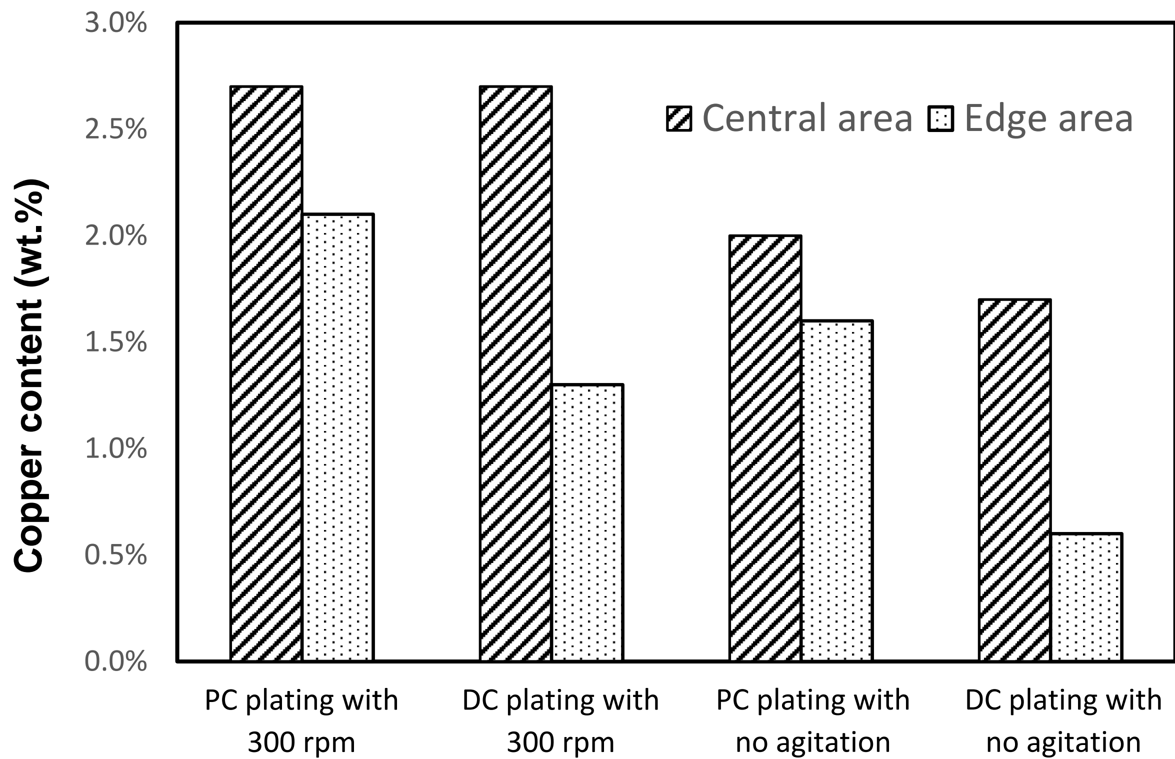
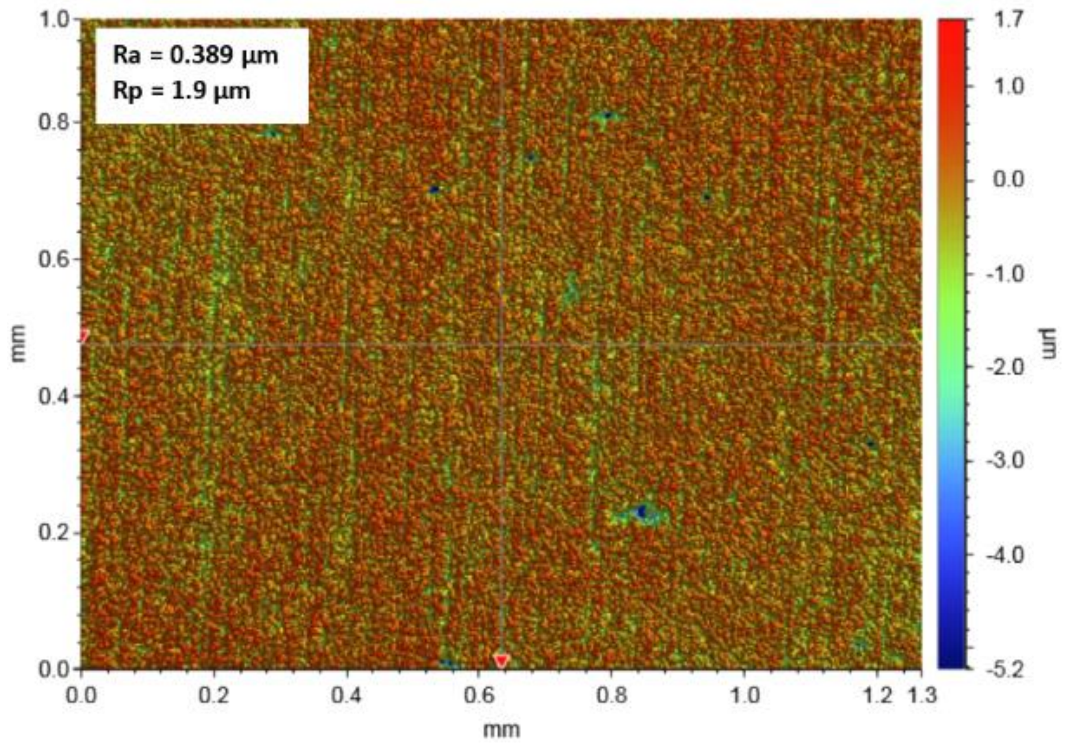


Figure 6

a)



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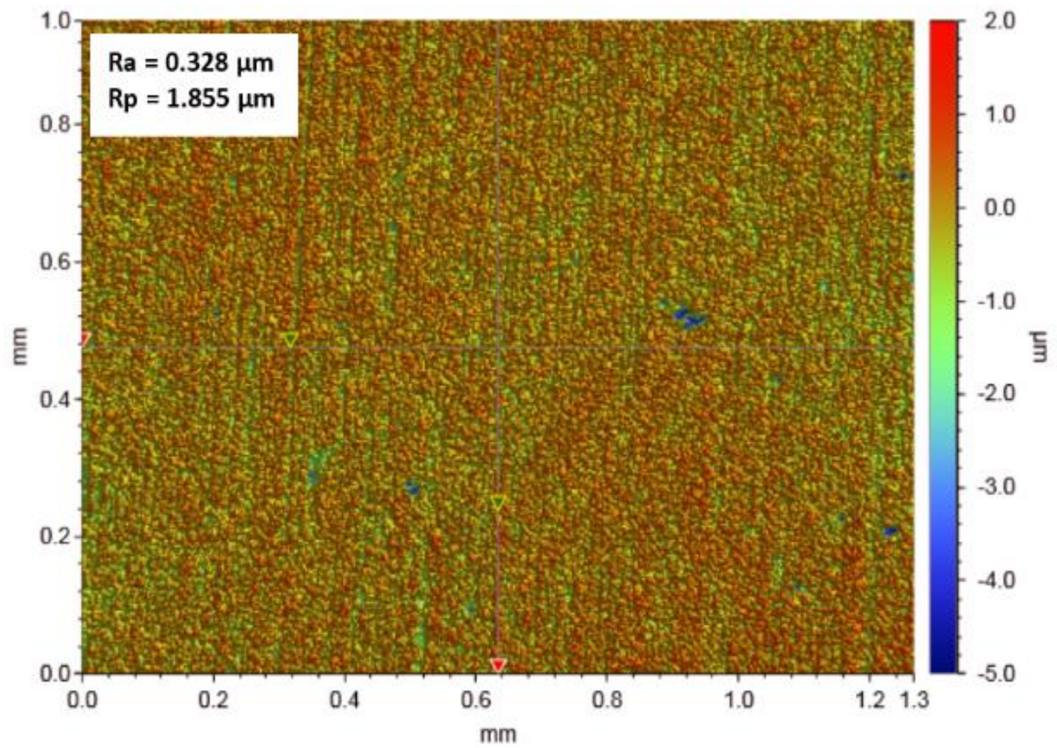

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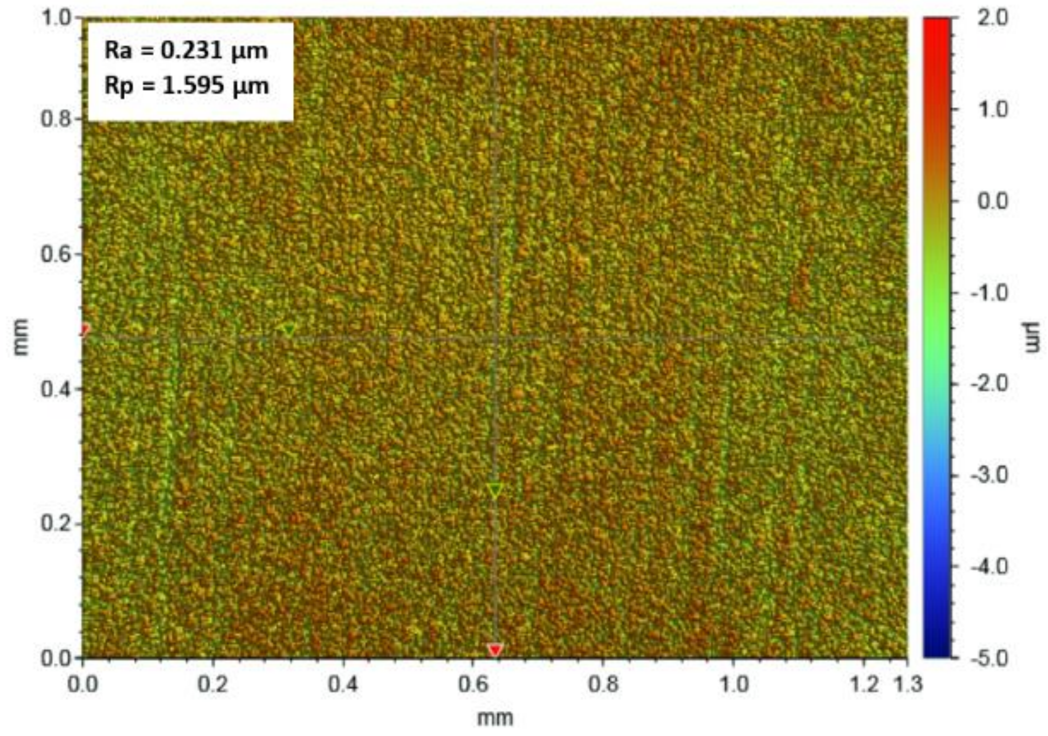

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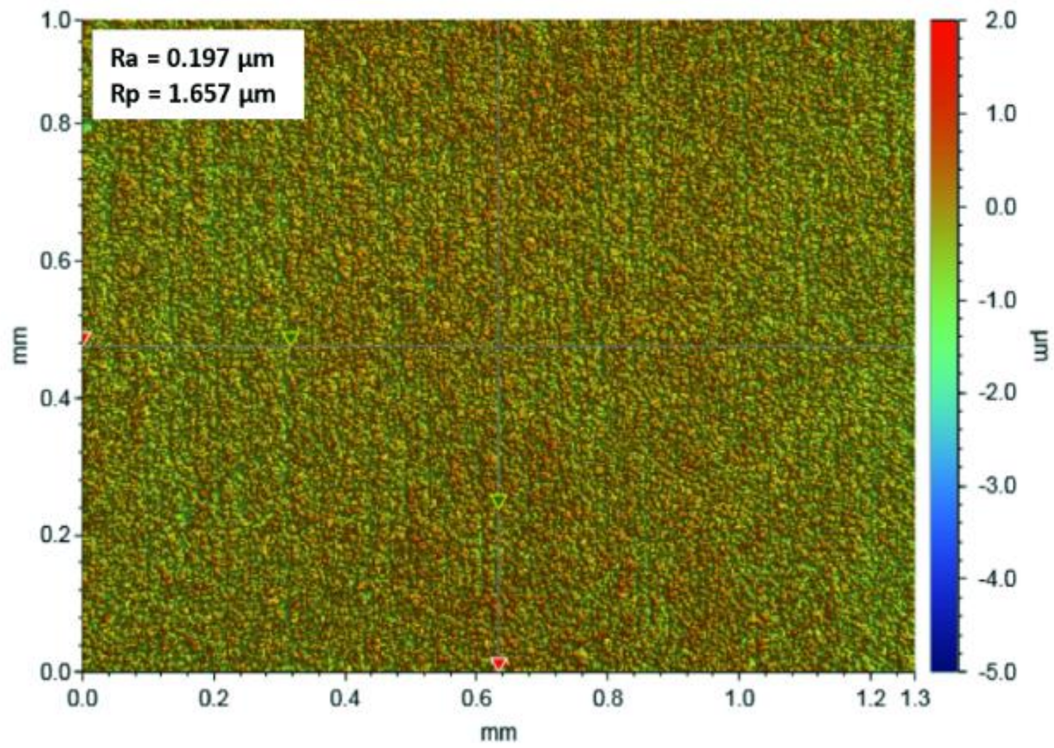

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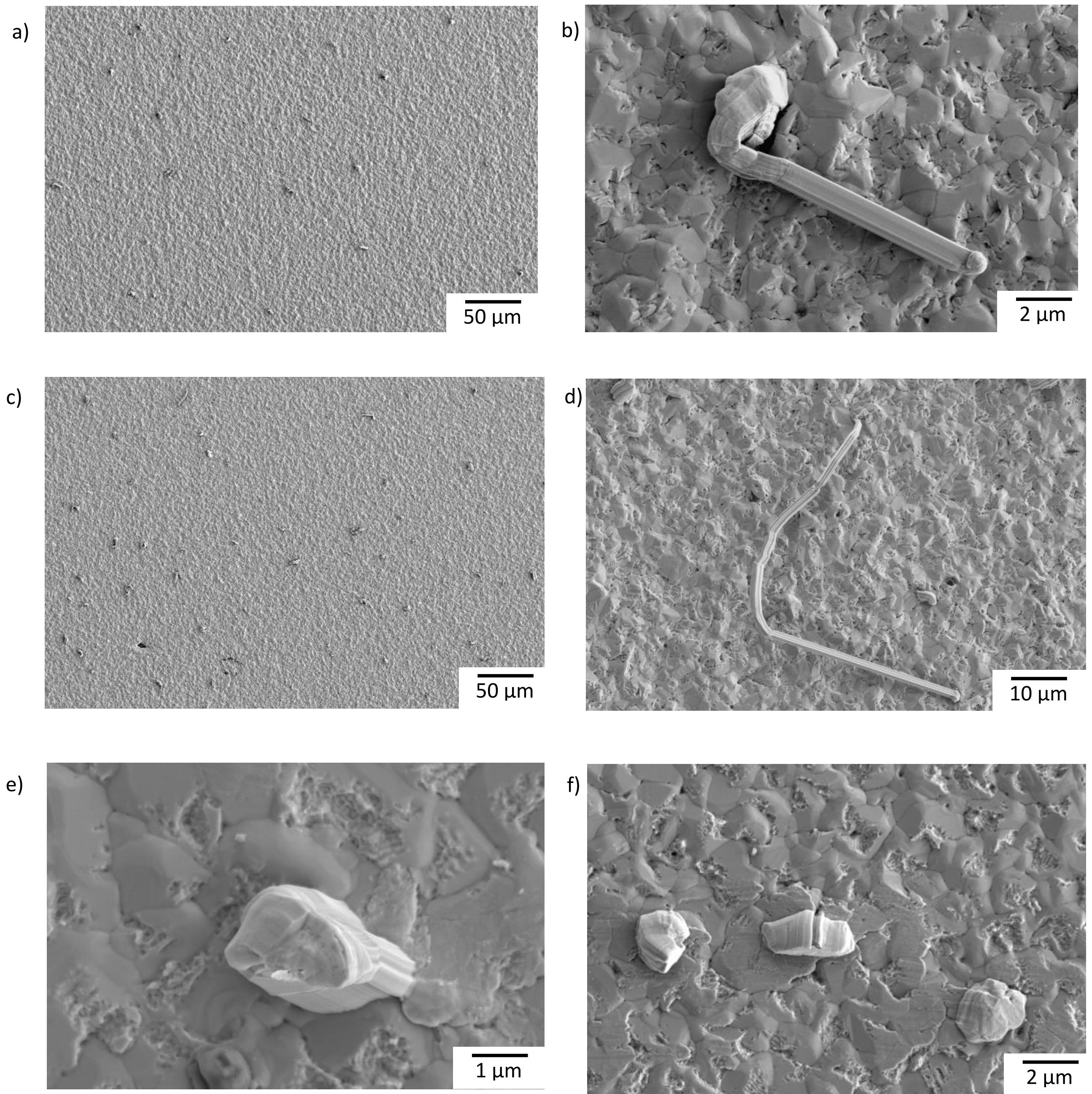
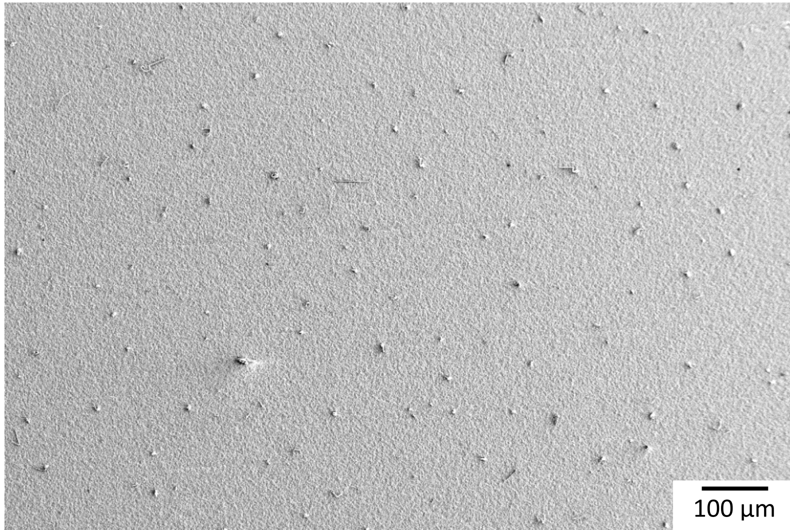


Figure 8

a)

b)



c)

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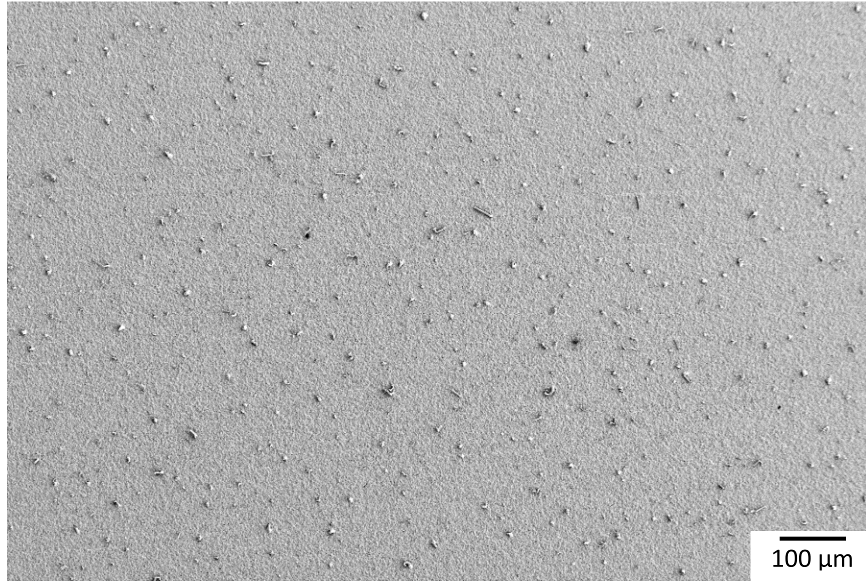

Figure 9