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Effect of the Diffusion Rate of the Copper Ions on the Co-electrodeposition of Copper and Nickel

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This study experimentally analyzed the influence of the diffusion rate of Cu ions on the growth of microstrucutres during the co-electrodeposition of copper and nickel. To change the diffusion rate of the Cu ions resolved in the electrodeposition solution, electrodeposition was performed under three different stirring conditions (0, 150, 300 rpm). The microstructure grew in an orientation vertical to the microstructure, similar to a probe without stirring, while a popcorn-shaped cluster with electrodeposition particles at the upper part of the microstructure was found under the stirring condition. Forced circulation of the electrodeposition solution by stirring drastically enhanced the movement of the Cu ions, and popcorn shaped clusters are formed. The average height and width of the structure electrodeposited for 20 minutes through stirring at 300 rpm were 1.5 and 4.3 times greater, respectively, than those of the structure electrodeposited without stirring. The substrate surfaces covered with electrodeposited microstructures were modified to be superhydrophobic by coating them with hydrophobic plasma polymerized fluorocarbon (PPFC).

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1. Introduction

Micro-nano structured surfaces made with electrodeposition can be applied to diverse fields such as surface modification, chemical sensors, various electrical devices, electrodes and catalysts.[1-5] Methods to form a micro-nano structure include bulk micromatching, electrodeposition after forming a pattern through surface micromatching,[2,3] or direct plating of a variety of metals growing dendritically on a substrate without forming a pattern.[6-11]

The method to perform electrodeposition after forming a pattern enables the easy fabrication of micro-nano structure. Moreover, these methods have a significant advantage in that a microstructure can be produced on the curved surface.[11] Therefore, many researchers are investigating methods to form a micro-nano structure with electrodeposition only and without forming a pattern. Representative methods in this area would be to plate a metal with dendrite growth singularly or as an alloy,[7-10] and to add the metal for electrodeposition and additives into an electrolyte to enable the metal to grow with crystals of a specific shape.[12,13]

In particular, a microstructure made with Cu-Ni alloy electrodeposition can not only be used as a catalyst for fuel cells, an electrode for a sensor or as a chemical sensor, but it can also be applied to the fabrication of porous microstructures or structures like nano tubes, making it the most actively studied method of electrodeposition nowadays.[14-17]

Because Cu is a more noble metal than Ni, when Cu and Ni are mixed for electrodeposition, Cu electrodeposition becomes relatively dominant.[15,16,19] Some studies have investigated methods to adjust the composition ratios of Cu and Ni for co-electrodeposition by mixing Ni electrolytes in high concentration and Cu electrolytes in low concentration, and by controlling the charge transfer rate in Cu-Ni co-electrodeposition.[14-16,19] When Cu electrolytes in low concentration and Ni electrolytes in high concentration are mixed for electrodeposition, Ni electrodeposition is controlled by charge transfer, while Cu electrodeposition is controlled by the diffusion of Cu ions. Therefore, when the charge transfer rate goes up, the amount of Ni electrodeposition increases in proportion. However, the diffusion rate of Cu ions does not change, even if the charge transfer rate increases, which indicates that the amount of Cu electrodeposition is disproportional to the charge transfer rate.[14-16] Consequently, the electrodeposition ratios of Cu and Ni can be controlled by adjusting the charge transfer rate when electrodeposition is performed by mixing the Ni electrolyte in high concentration and the Cu electrolyte in low concentration.

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In an electrodeposition solution in which low concentration Cu and high concentration Ni are mixed, Cu electrodeposition forms spherical particles, while Ni is electrodeposited by surrounding these spherical particles.[14-16] Here, the size of the spherical particles is proportional to the concentration of Cu. However, what causes the varying composition ratios of Cu and Ni is either on the growth mechanism of the microstructure being formed as a result of the Cu-Ni alloy electrodeposition or the location of the electrodeposited substrate not being clearly identified, which has been a subject of speculation until now.[7,15,18]

Therefore, this study aimed to identify the growth mechanism of the microstructure in Cu-Ni alloy electrodeposition and the causes of varying compositions of Cu and Ni based on the location of the micro-structured surface. Since the single biggest influential factor on the growth of a microstructure is the diffusion of Cu ions, the electrodeposition solution was stirred in order to deliberately increase the diffusion of Cu ions. Therefore, it is possible to identify the cause of varying composition ratios of Cu and Ni depending on the growth mechanism of the microstructure and the location of the electrodeposited substrate by adjusting the diffusion rate of Cu ions. In addition, to investigate the applicability of Cu-Ni composite electrodeposition, fabricated sample surfaces are coated with hydrophobic plasma-polymerized fluorocarbon (PPFC) of and applied to modify superhydrophobic surfaces.

2. Experimental

In order to form a microstructure by using Cu-Ni alloy electrodeposition, a three-electrode system (Princeton Applied Research, USA) was utilized for electrodeposition. A silicon substrate the size of 1×1 cm^2 to which Cr (100 nm)/Cu (100 nm) is deposited consecutively was used as a working electrode of the three-electrode system. A platinum mesh the size of 2.5×2.5 cm^2 (i-Nexus, USA) was used as the counter electrode, and an Ag/AgCl electrode (Metrohm, Switzerland) was used as the reference electrode.

The Cu-Ni electrodeposition solution is comprised of 1 M Ni $(NH_2SO_3)_2$ (Dischem, USA), 0.02 M $CuSO_4$ (Dischem, USA), and 0.26 M H_3BO_3 (Dischem, USA) as a pH buffer. The alloy electrodeposition was performed at a constant voltage of -1.0 V. It was carried out under the three different stirring conditions (0, 150, 300 rpm) and the three different durations of electrodeposition (2, 10, 20 min). For stirring, a magnetic stir bar (Cowie technology, UK) whose diameter is 0.8 cm and length is 3.8 cm was used.

A scanning electron microscope (SEM) device (S-4800, HITACHI, Japan) was used to analyze the shape and size of the micro-structured surface. Meanwhile, an energy dispersive spectroscopy (EDS) device (7593-H EMAX, HORIBA, Japan) was employed to analyze the Cu-Ni composition ratios.

3. Results and Discussion

3.1 Cu-Ni Electrodeposition with No Stirring (0 rpm)

When no stirring was performed in the electrodeposition solution in which low concentration Cu and high concentration Ni are mixed, SEM images of the Cu-Ni electrodeposition structure over time are as shown in Fig. 1, and the Cu-Ni composition ratios based on the locations shown in Fig. 1 are listed in Table 1. From the results suggested in Fig. 1 and Table 1, the growth mechanism of Cu-Ni electrodeposition structure can be analyzed as follows. First, as shown in Fig. 2(a), the Cu content varies depending on the location of analysis, and it is the highest at the upper part (F) of the microstructure. Higher Cu contents can also be found at the bottom surface (H), which is far from the structure, than the bottom surface (G) close to the structure. This result is attributable to the extraction of the Cu ions that exist in the electrodeposition solution at a location within closer reach from the surface of the substrate.

As shown in Fig. 3(a), the Cu ions within the ranges of R1 and R2 are located close to the upper part of the electrodeposited structure, and as such, they are more likely to be electrodeposited at the upper part of the electrodeposited structure, while those Cu ions out of the aforementioned ranges are more likely to be electrodeposited on the

Table 1 Cu-Ni composition ratio obtained by the EDS measurement at each area marked in Figs. 1 and 4

	Position	Composition ratio Cu : Ni [at.%]	Position	Composition ratio Cu : Ni [at.%]
No stirring	A	54.74 : 45.26	E	18.49 : 81.51
	B	29.46 : 70.54	F	90.65 : 9.35
	C	77.52 : 22.48	G	4.37 : 95.63
	D	14.20 : 85.80	H	17.31 : 82.69
Stirring (150 rpm)	I	63.05 : 36.95	L	18.47 : 81.53
	J	41.81 : 58.19	M	94.51 : 5.49
	K	91.11 : 8.89	N	10.88 : 89.12

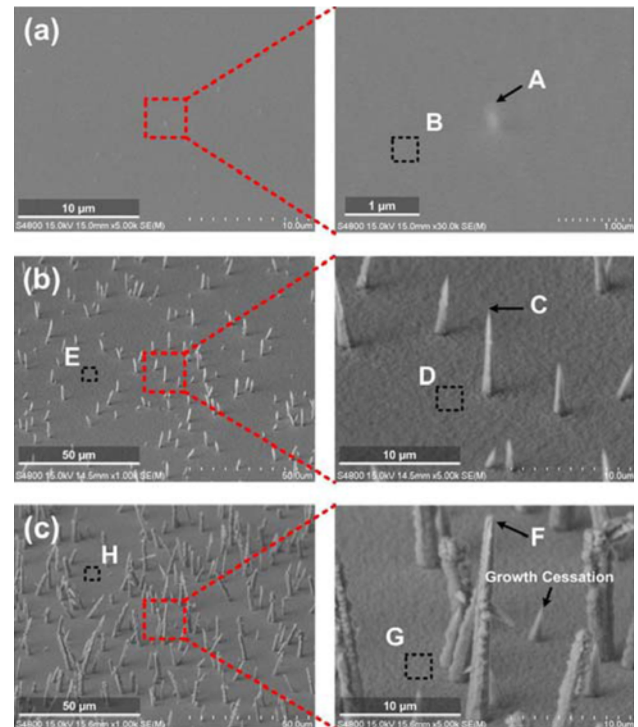

Fig. 1 SEM images of the surfaces electrodeposited without stirring at potential -1.0 V with different electrodeposition times: (a) 2 min, (b) 10 min, and (c) 20 min

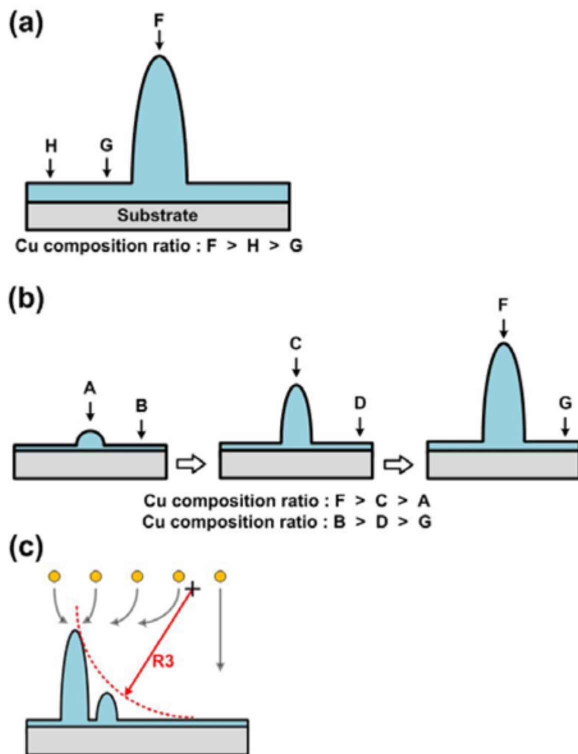

Fig. 2 (a) Cu composition ratio according to the position of the microstructured surface, (b) Cu composition ratio according to the electrodeposition time, and (c) growth cessation of the short microstructure that stands near the tall microstructure

substrate as they are more closely located to the substrate plane. Therefore, the Cu composition ratio is the lowest at a point (* area) where the structure and the bottom meet each other. This is also where the diffusion distance of the Cu ions is relatively long. Subsequently, the radius within which the Cu ions can be diffused to reach the substrate surface like R1 and R2 is called the diffusion radius.

Secondly, as shown in Fig. 2(b), as the electrodeposition structure grows, the Cu content at the same point changes. The greater the height of the electrodeposition structure was, the greater the Cu content became at the upper part of the structure: A(54.74%) < C(77.52%) < F(90.65%). In contrast, the Cu composition ratio on the bottom surface close to the structure decreased when the structure became taller: B(29.46%) > D(14.20%) > G(4.37%). As shown in Fig. 3(a), the diffusion radius became bigger with a taller structure (R2 > R1), and as such, the amount of Cu ions (Cu ions contained in the hatch area) within the radius of diffusion increased. Therefore, the bigger the structure was, the larger the amount of Cu extracted from the upper part of the structure relatively became. On the contrary, the distance between the circumference made with the diffusion radius and the point where the structure touches the ground (S2) became bigger when the size of the structure became greater.

Therefore, the bigger the structure is, the number of Cu ions that can be diffused to the point where the structure touches the ground diminishes. One example to demonstrate the validity of this analysis would be that a small structure in close proximity to a bigger structure stops growing, as shown in Fig. 1(c). If the small structure located near the bigger structure fails to be included in the diffusion radius (R3) as

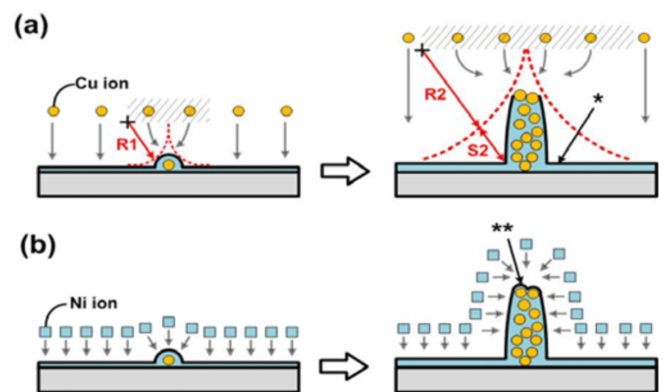

Fig. 3 Dominant electrodeposition factor of each metal in the Cu-Ni electrodeposition: (a) diffusion rate of Cu ions in Cu electrodeposition, (b) charge quantity supplied on the deposited surface in Ni electrodeposition

shown in Fig. 2(c), the structure concerned stops growing.

Thirdly, the electrodeposited structure grows in an orientation vertical to the substrate. While the Cu electrodeposition is controlled by diffusion, the Ni electrodeposition is controlled by the charge transfer, as shown in Fig. 3(b). In this study, in particular, because the electrodeposition solution consisted of highly concentrated Ni ions, the Ni electrodeposition was not affected by diffusion. As such, the Ni electrodeposition was carried out evenly all over the substrate. Therefore, the Ni ions were extracted from the surface of the Cu electrodeposited material formed either at the upper part of the electrodeposited structure (** area), or from the side of the electrodeposited structure. With a combination of the Cu particles extracted in concentration on the upper part of the electrodeposited structure and the Ni extracts encasing them, the micro electrodeposited structure grew in an orientation vertical to the substrate.

3.2 Cu-Ni Electrodeposition with Stirring (150, 300 rpm)

The SEM images of the Cu-Ni alloy electrodeposition structure when the Cu-Ni electrodeposition solution was stirred at 150 rpm and 300 rpm are shown in Figs. 4 and 5, and the Cu/Ni content at each point is as shown in Table 1. Compared to the results of electrodeposition under an unstirred condition, it can be seen that more electrodeposition cores were generated under the stirred condition (Fig. 4(a) and Fig. 5(a)). Compared to the density of the microstructure electrodeposited for 10 minutes under the unstirred condition (Fig. 1(b)), the density of the structure electrodeposited under the condition of stirring at 150 rpm (Fig. 4(b)) was about three times greater. This is because the probability of the Cu ions coming in contact with the surface of the substrate was greater due to the forced stirring of the electrodeposition solution.

Unlike the shape of the microstructure growing in a vertical orientation under the unstirred condition, round electrodeposition particles were clustered at the upper part of the microstructure under the stirring condition (Fig. 4(b), (c) and Fig. 5(b), (c)). This cluster of electrodeposition particles was also attributable to the rate of Cu ion diffusion resulting from stirring. The Cu composition ratio (Point K, 91.11%) measured at the upper part of the structure electrodeposited for 10 minutes with stirring at 150 rpm was higher than that (Point C, 77.52%) at the upper part of the vertical structure electrodeposited for

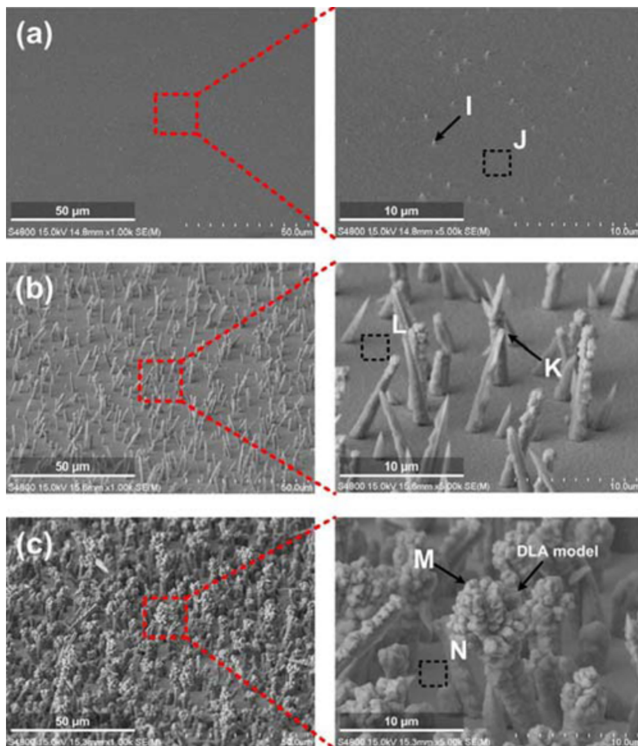

Fig. 4 SEM images of the surfaces electrodeposited with stirring (150 rpm) at potential -1.0 V with different electrodeposition times: (a) 2 min, (b) 10 min, and (c) 20 min

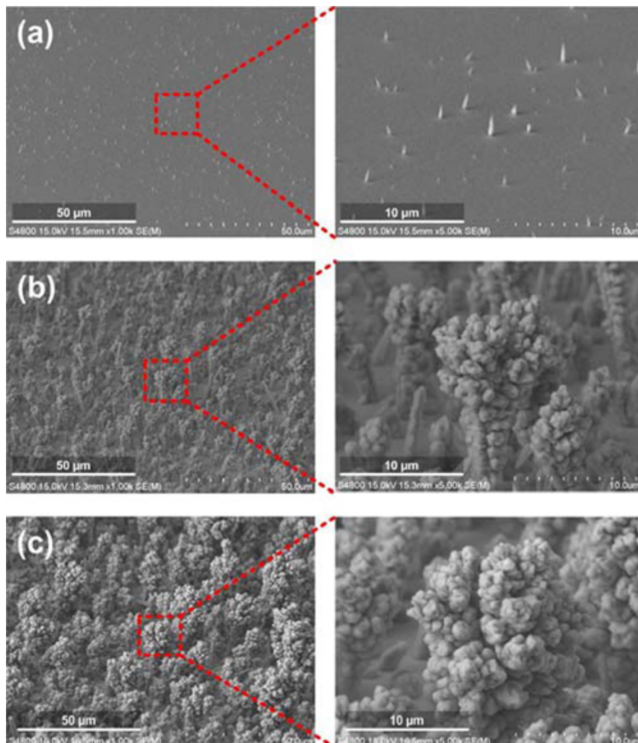

Fig. 5 SEM images of the surfaces electrodeposited with stirring (300 rpm) at a potential -1.0 V with different electrodeposition times: (a) 2 min, (b) 10 min, and (c) 20 min

10 minutes without stirring. As shown in Fig. 4(b), a cluster of electrodeposition particles began to form at the upper part of the structure electrodeposited for 10 minutes with stirring at 150 rpm. This Cu ion composition ratio rose even higher to 94.51% at Point M in Fig. 4(c), which was electrodeposited for 20 minutes.

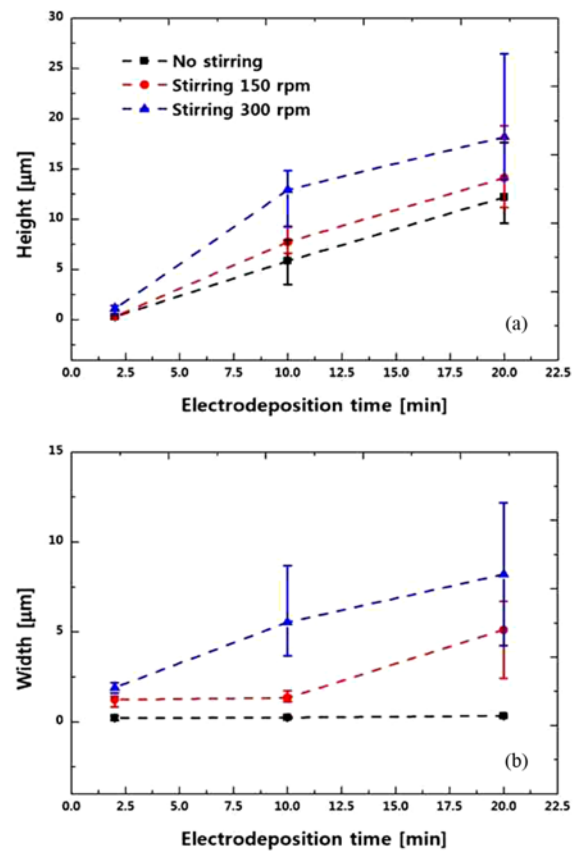

Fig. 6 Size comparison of the electrodeposited microstructures in terms of the stirring condition: (a) height and (b) width of the microstructures

The Cu composition ratio was found to be particularly high from the cluster of electrodeposited particles. An increase in the amount of Cu electrodeposition when it is performed at a constant voltage as in this study, led to a decrease in the amount of Ni electrodeposition. This is because the total amount of Ni and Cu electrodeposition was controlled by the size of the applied voltage. Therefore, provided that the electrodeposition is performed at the same voltage, if the amount of Cu electrodeposition increased, the amount of Ni electrodeposition decreased. Due to the excessively fast diffusion rate of the Cu ions resulting from the stirring of the electrodeposition solution, spherical particles consisting of Cu properties formed in large numbers at the upper part of the electrodeposited structure, which grew in a vertical orientation.

With an increase in the amount of Cu electrodeposition, the amount of Ni electrodeposition diminished, making it impossible for Ni to fully cover the spherical particles of Cu properties. As a result, a cluster structure to which spherical particles are clinging formed. This cluster structure is consistent with the diffusion limited aggregation (DLA) structure.[11,20] As shown in Fig. 6, the average height and weight of the structure electrodeposited for 20 minutes with stirring at 300 rpm is 1.5 and 4.3 times greater than those of the electrodeposited structure without stirring, respectively. Because the cluster increases the width of the electrodeposited structure dramatically, one can see that a popcorn

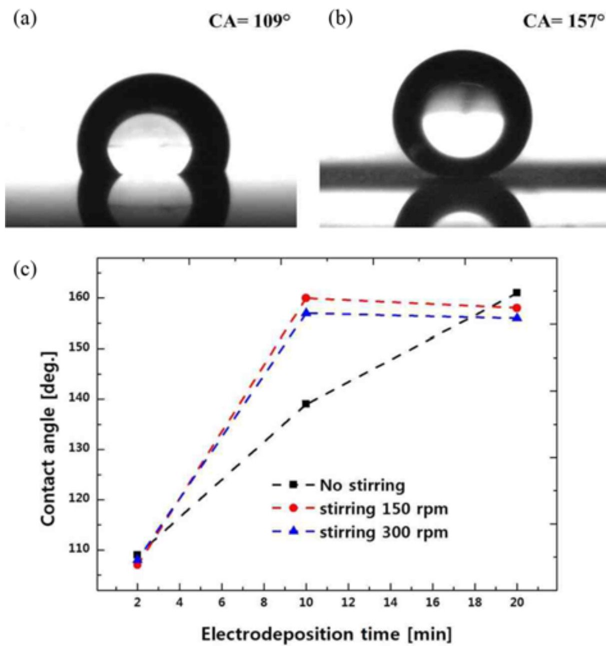

Fig. 7 Water drop images on each surface electrodeposited for (a) 2 min and (b) 10 min, and (c) the change of contact angle according to the electrodeposition time for three different stirring conditions

shaped cluster covers the substrate surface almost entirely for a structure electrodeposited for 20 minutes at 300 rpm (Fig. 5(c)). Forced circulation of the electrodeposition solution by stirring drastically enhances the movement of the Cu ions compared to pure diffusion in non-stirring condition. The amount of electrodeposited Cu is substantially increased due to the Cu ions delivered by the circulation. Therefore, popcorn shaped clusters are simply formed under the stirring conditions.

3.3 Application: Microstructured Superhydrohobic Surface

The fabricated substrate covered with electrodeposited microstructures were coated with PPFC of a hydrophobic nature and applied to modify superhydrophobic surfaces. To investigate the change in the degree of hydrophobicity according to electrodeposition time and the use of stirring, the contact angles of the fabricated samples were measured using a contact angle meter (SEO Phoenix series, Korea). Deionized (DI) water used for the measurement of the contact angles, and the volume of the water droplet was 4 μl. The measured contact angle was the average obtained from five measurements.

The contact angle dramatically increased from 109° (electrodeposition time of 2 min, Fig. 7(a)) to 157° (10 min, Fig. 7(b)) with stirring at 300 rpm. During the Cu-Ni composite electrodeposition process, the substrate surface was thus modified and became a superhydrophobic surface. As shown in Fig. 7(c), while the contact angles of the samples fabricated in an unstirred condition gradually increases according to the electrodeposition time, those of the samples fabricated in the stirred conditions abruptly increases and approach around 160° at the relatively short electrodeposition time of 10 min. A proper structure density and height are required to lift a water droplet completely on the top of the microstructures.[21] As shown in Fig. 6, the heights and widths of the microstructures increase more rapidly in the stirring condition than in the non-stirring condition. As a result, the stirring condition produced superhydrophobic surfaces more quickly than the non-stirring condition. However, after electrodeposition for 20 min, the contact angles of samples fabricated in the stirring conditions decreased. This was attributed to the increase in the contact area between the water drop and the popcorn-shaped, clustered structure.

4. Conclusions

This study examined the effect of the diffusion of Cu ions in an electrodeposition solution in which low-concentration Cu and high-concentration Ni were mixed on the formation of a microstructure. In addition, it identified the cause of varying Cu-Ni composition ratios, which depended on the growth mechanism of the Cu-Ni microstructure and the location of the microstructured electrodeposition surface. To change the diffusion rate of the Cu ions dissolved in the electrodeposition solution, electrodeposition was performed under three different stirring conditions (0, 150, 300 rpm). Without stirring, the Cu ions were electrodeposited in high concentration at the upper part of the microstructure with a short ion diffusion distance, while Ni electrodeposition took place evenly all over the working electrode, including the structure formed. Because the Cu ions diffusion radius increased with a greater height of the microstructure, the Cu content increased with a greater height of the structure. On the contrary, the plate near the microstructure had lower Cu composition ratios with a greater structural height. Because the Cu electrodeposition took place in concentration at the upper part of the microstructure, the electrodeposition structure grew in an orientation vertical to the substrate like a probe.

When the Cu-Ni electrodeposition solution was stirred at 150 rpm, electrodeposition cores were formed with a density nearly three times higher than the unstirred condition. Moreover, the microstructure grew in an orientation vertical to the microstructure like a probe without stirring, while a popcorn-shaped cluster with electrodeposition particles at the upper part of the microstructure was found under the stirring condition. The Cu composition ratios measured at the electrodeposition particle cluster indicated that this electrodeposition particle cluster is also attributable to the increased diffusion rate of Cu ions from stirring. Due to the formation of the cluster, which resulted from excessive Cu electrodeposition, the average height and width of the structure electrodeposited for 20 minutes through stirring at 300 rpm were 1.5 and 4.3 times greater, respectively, than those of the structure electrodeposited without stirring. While the contact angles of the samples fabricated in the non-stirring condition gradually increases according to the electrodeposition time, those of the samples fabricated in the stirring conditions abruptly increases and approach around 160° at the relatively short electrodeposition time of 10 min. The stirring condition produced superhydrophobic surfaces more quickly than the non-stirring condition.

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