Int. J. Electrochem. Sci., 12 **(2017)** 4714 – 4723, doi: 10.20964/2017.06.78

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Cu–W Thin Film Electrodeposited in an Aqueous Solution

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Received: 21 March 2017 / *Accepted:* 23 April 2017 / *Published:* 12 May 2017

Cu-W thin films were electrodeposited on indium tin oxide (ITO) glass substrates in an aqueous solution using a rectangular pulse current technique in a range of frequency from 0.2 MHz to 1 MHz. The W concentration in the Cu-W thin film measured with energy dispersive X-ray spectroscopy (EDX) was dependent on an amplitude and frequency of the rectangular pulse current. The maximum W concentration in the Cu-W thin film was 9 wt. %. X-ray diffraction (XRD) revealed that the Cu-W thin film had crystallographic planes parallel to the ITO glass substrate such as (111), (200), (220), and (311) planes. Surface images of the Cu-W thin film observed with scanning electron microscope (SEM) showed an aggregation of an island called a nano cauliflower. These experimental results indicate that the Cu-W thin film was an alloy comprising copper and tungsten, and that tungsten was electrodeposited in the aqueous solution free of the iron-group element.

Keywords: Cu-W thin film; aqueous solution; megahertz; nano cauliflower; iron-group element

1. INTRODUCTION

Electrodeposition of tungsten in an aqueous solution is well known to require co-deposition of the iron-group element such as Fe, Co, and Ni, which is called the induced co-deposition [1]. Many mechanisms have been proposed to explain the induced co-deposition [2-3]. However, we are far from complete understanding. For example, a negative sodium tungstate dehydrate that is usually used is needed to approach an electrical double layer to receive an electron from a cathode electrode regardless of a homogeneous or heterogeneous reaction [4]. The proposed scenarios cannot explain why the negative sodium tungstate dehydrate approaches the cathode electrode against the applied potential, and the electron transfers the negative sodium tungstate dehydrate against the repulsive coulomb interaction.

On the other hand, electrodeposition of tungsten in a molten salt [5-6] has attracted researchers because of its easy preparation, stability, and non-volatility except for the high deposition temperature. The pure tungsten was reported to be electrodeposited on a substrate.

With respect to the induced co-deposition with the iron group element in the aqueous solution, there have been many studies on Ni-W thin films [7-11] and Co-W thin films [12-15]. In the Ni-W electrodeposition, a citrate compound was employed as a complexing agent. The effects of electrochemical parameters such as an additive, PH, temperature, current density, and deposition technique on the concentration of W in the deposited film were widely investigated to increase the concentration of W. As a result, the maximum W concentration was reported to be 58.4 wt. % [7]. In the Co-W electrodeposition, several kinds of complexing agents and levelling agents were used to increase the W concentration and to obtain smooth surfaces. The maximum content of W in the Co-W thin film was 53 wt. % [13].

The co-deposition of Cu and W in the aqueous citrate solution free of the iron group element [16] has recently been reported. The maximum W concentration was 26 wt. %. This was the first study on the W deposition with the non-iron group element.

We also reported the co-deposition of Cu and Mo from a viewpoint of energy transfer transition [17]. If an applied electric field provides the energy to transit an electron in the electrode at the Fermi level to the energy level of a metal ion in the aqueous solution, the electron will transfer the quantized rotational energy level of the ion. In fact, a resonant frequency at which a deposit mass drastically increases, and a resonant frequency spacing between the neighboring resonant frequencies were found [18]. A rectangular pulse current having a frequency of megahertz was applied to provide the energy by which the electron can transfer. This is our motivation for the present study in which the rectangular pulse current having a frequency of megahertz will make it possible to generate the deposition of W in the aqueous solution.

The present study aims at demonstrating that the Cu-W thin film generated in the aqueous solution that does not include the iron group element is an alloy comprising Cu and W.

2. EXPERIMENTAL SETUP

The aqueous solution including chemical compounds (mol L^{-1}): $CuSO_4 \cdot 5H_2O$, 0.945; $KNaC_4H_4O_6 \cdot 4H_2O$, 0.65; and $Na_2WO_4 \cdot 2H_2O$, 0.5, or 0.75, was prepared. The aqueous solution was strained with a membrane (pore size 0.1 μm) to remove copper hydroxide in the aqueous solution.

The ITO glass (sheet resistance 7Ω) of 15 x10 mm^2 and a carbon plate of 50x40 mm^2 were prepared for a cathode and an anode electrode. The two electrodes were set parallel to each other in an electrochemical cell filled with the aqueous solution.

Electrodeposition was performed using the rectangular pulse current having a frequency from 0.2 MHz to 1.0 MHz, which was provided with a function generator (NF Corporation WF1965). A metal film resistor was connected in series with the electrochemical cell so as to calculate the current density flowing in the electrochemical cell. The impedance of the metal film is stable irrespective of the frequency below 80 MHz. Figure 1 shows the typical rectangular pulse current having an amplitude of 13 mA/cm^2 and a frequency of 0.5 MHz in the aqueous solution including 0.75 mol/L sodium tungstate dehydrate. The on-time of the rectangular pulse current was chosen to be equal to the off-time of the rectangular pulse current.

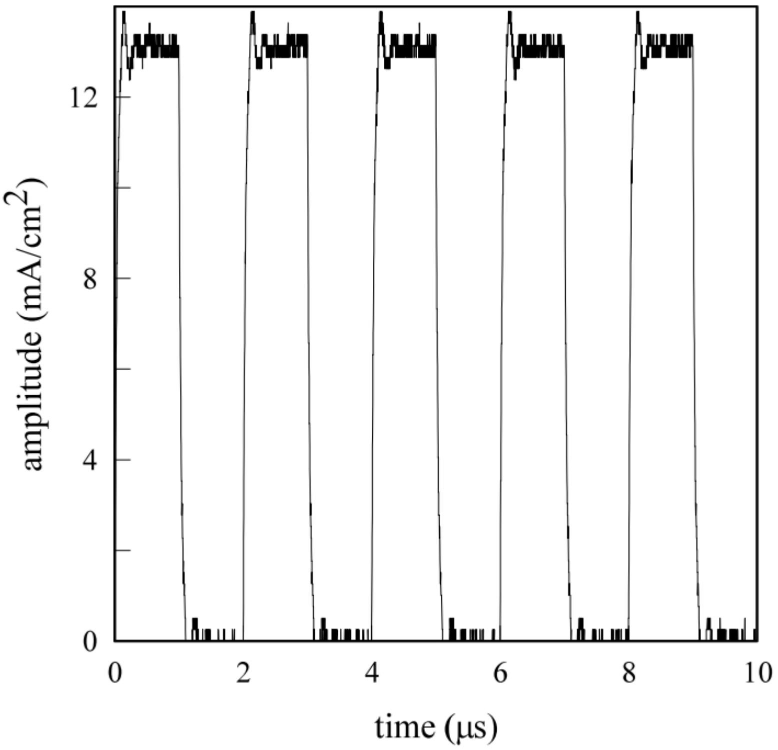

Figure 1. Rectangular pulse current having an amplitude of 13 mA/cm^2 and a frequency of 0.5 MHz in the solution including 0.75 mol/L sodium tungstate dehydrate.

All the Cu-W films were electrodeposited at a temperature of 300 K. The concentration of W contained in the Cu-W thin film formed on the ITO glass was measured with EDX (Shimazu EDX-800). XRD with CuKα radiation (Rigaku Ultima) determined a crystallographic structure of the Cu-Mo-Al thin film. The surface of the Cu-W thin film was observed with SEM (Hitachi TM3030).

3. RESULTS AND DISCUSSION

The W concentration in the Cu-W thin film dependent on an amplitude of the rectangular pulse current can be derived using the Butler-Volmer equation [19-20]. The impedance of the electric double layer at the anode electrode, and the impedance of the solution between the two electrodes can be ignored because the concentrations of the three chemical compounds are very high and the area of the anode electrode is 27 times larger than that of the cathode. Hence, we consider only the electric potential applied to the cathode potential. Using the Butler-Volmer equation that does not include the effect of the resonant electrodeposition [17-18], the concentration of W in the Cu-W thin film, P_W has the form,

$P_W = \frac{j_W}{j_{Cu}+j_W}$, (1)

where $j_i = j_{oi} exp\left(-\frac{\alpha_i m_i F \eta_i}{RT}\right)$, (2)

and $\eta_i = E - E_i,\ i = W\ or\ Cu.$ (3)

Here, j_i is the current density due to the crystallization of ion i, j_{oi} is the exchange current density, α_i is the transfer coefficient, m_i is the ionic charge, F is the Faraday's constant, T is the absolute temperature, R is the gas constant, E is the potential applied to the electric double layer at the cathode, and E_i is the equilibrium potential at the cathode. When the amplitude of the total current density flowing in the electrochemical cell is set to i_o, the derivative of Eq. (1) with respect to i_o becomes,

$\frac{d}{di_o}\left(\frac{j_W}{j_{Cu}+j_W}\right) = \frac{2FZ}{RT}\frac{j_{Cu}j_W(3\alpha_W-\alpha_{Cu})}{(j_{Cu}+j_W)^2}$, (4)

where Z is the impedance of the electric double layer at the cathode. The value of the transfer coefficient is between 0 and 1 [21]. The apparent transfer coefficient has a value beyond 1 [22]. The transfer coefficient will be dependent on the frequency f of the rectangular pulse current and the ion concentration c_i in the solution, but the details are unknown. Eq. (4) concludes,

(1) when $3\alpha_W(f, c_W) > \alpha_{Cu}(f, c_{Cu})$, the W concentration in the Cu-W thin film increases with the total current density,

(2) when $3\alpha_W(f, c_W) < \alpha_{Cu}(f, c_{Cu})$, the W concentration in the Cu-W thin film decreases with the total current density.

The extended Butler-Volmer equation for the multistep reaction [22] is known and the transfer coefficient also has an extended form, however, for simplicity, we assume the single step reaction for Cu^{2+} and W^{+6} and the reaction time much faster than a microsecond. In addition, if electrodeposition occurs resonantly, the electrodeposited masses of Cu and W rapidly increase at the resonant frequency [18]. Hence, the W concentration in the Cu-W film is expected to behave complicatedly. In fact, both cases (1) and (2) will appear in the next chapter.

3.1 Cu-W thin film electrodeposited in the 0.5 mol/L sodium tungstate dehydrate solution

Figure 2 shows the W concentration in the Cu-W thin film. The deposition of W indicates that the reaction times of several electrochemical reactions proposed in [2-3] should be much faster than a microsecond. In addition, whether or not the electron transfer reaction is homogeneous or heterogeneous [4], the proposed model should provide two understood interpretations, one is why the minus ions can exist in the electric double layer under the electric potential, the other is why the minus ion can receive the electron.

As shown in Fig. 2, the W concentration changes with the frequency. We have reported that a change in the Mo concentration in the Cu-Mo thin film with frequency might correspond to a change in the mass deposited at the resonant frequency [17]. If the deposition occurs resonantly in the frequency range from 0.2 to 1 MHz, the deposition masses of Cu and W periodically change with the frequency as shown in the Ni electrodeposition [18]. In the framework of the energy level transition, electrodeposition is interpreted to obey the energy level between an electron at the Fermi energy level in the electrode and an ion characterized by the quantized rotational energy level. Several resonant frequencies at which the mass of Cu or W remarkably increases may exist. Hence, the W concentration in the Cu-Mo thin film changes with the frequency.

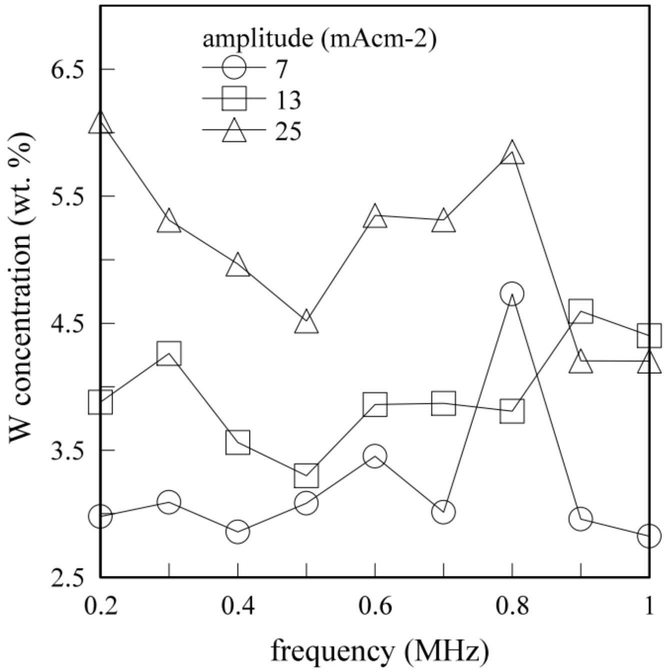

Figure 2. Frequency-dependence of the W concentration of the Cu-W thin film electrodeposited in the solution including 0.5 mol/L sodium tungstate dehydrate.

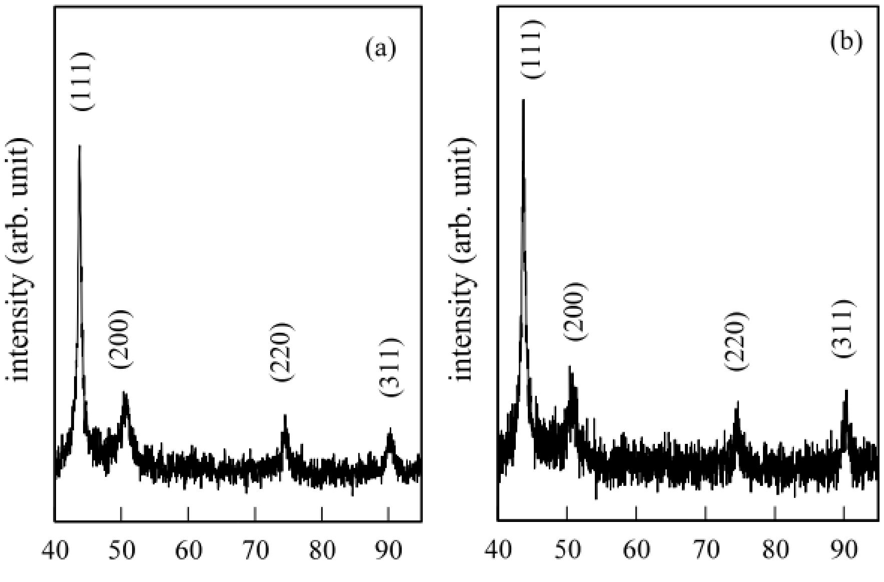

Figure 3. XRD charts of the Cu-W films electrodeposited in the solution including 0.5 mol/L sodium tungstate dehydrate at (a) an amplitude of 7 mA/cm^2 and a frequency of 0.8 MHz, and (b) at an amplitude of 25 mA/cm^2 and a frequency of 0.2 MHz. The Cu-W thin films of (a) and (b) had 4.7 μm and 4.9 μm in thickness.

The W concentration in the Cu-W thin film at the lower frequency increases with the current density. However, at the higher frequency, it does not always prove right. Following Eq. (4), this indicates that the W concentration is remarkably affected by the frequency owing to a small difference between $3\alpha_W$ and α_{Cu}. The maximum W concentration in the Cu-W thin film was 6 wt. %.

Figure 3 shows XRD charts for two kinds of the Cu-W thin films that indicate a maximum W concentration at a current density of 7 and 25 mA/cm^2. The diffraction peaks indexed as the (111), (200), (220), and (311) crystallographic planes are well consistent with those of polycrystalline copper [23]. These diffraction peaks also indicate that the crystallographic planes parallel to the ITO glass exist in the Cu-W thin film. As no other diffraction peaks are observed, the Cu-Mo thin film is concluded to be an alloy of Cu and W. Each diffraction peak in Fig. 3 is broad in width. Using the well-known Scherrer equation and [111] diffraction peak, the mean grain sizes of the Cu-W thin film in Figs. 3 (a) and (b) yield the same size as 13 nm.

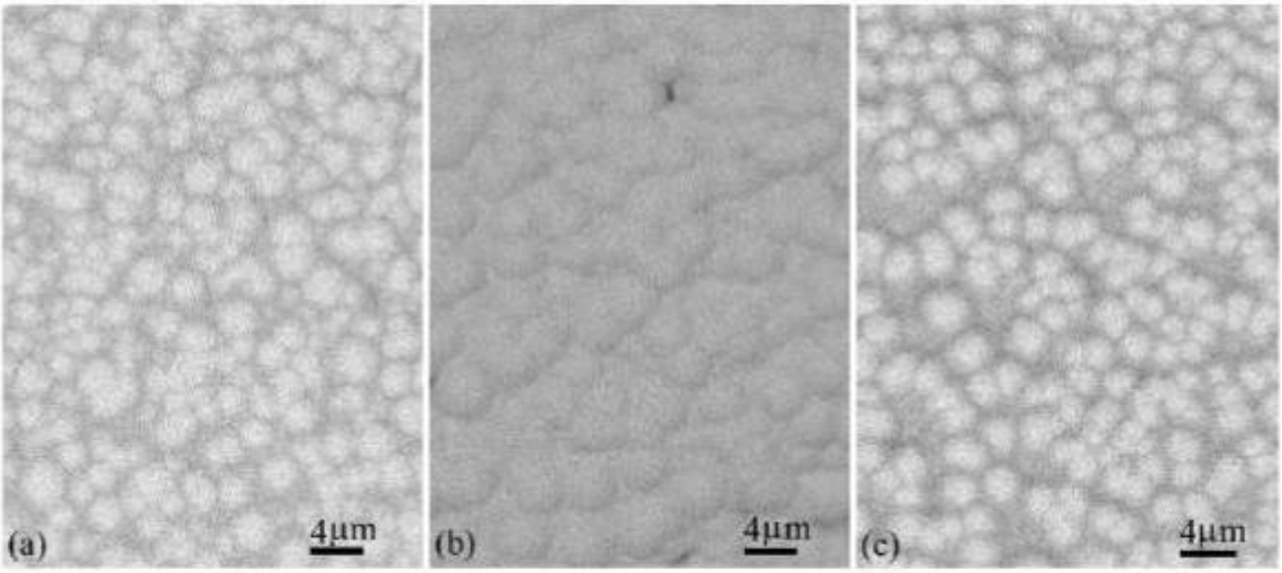

Figure 4. SEM images of the Cu-W films electrodeposited in the solution including 0.5 mol/L sodium tungstate dehydrate at (a) an amplitude of 7 mA/cm^2 and a frequency of 0.8 MHz, (b) at an amplitude of 13 mA/cm^2 and a frequency of 0.3 MHz, and (c) an amplitude of 25 mA/cm^2 and a frequency of 0.2 MHz. The Cu-W thin films had 2.4 μm in thickness.

Figure 4 shows SEM images of the Cu-W thin film. The Cu-W thin film consists of an island that has about 4 μm in size. The island comprises grains of 13 nm in size. The island is called a nano cauliflower [24] consisting of nanometer grains. The surface morphology is consistent with that observed in the Cu-Mo [17, 25].

3.2 Cu-W thin film electrodeposited in the 0.75 mol/L sodium tungstate dehydrate

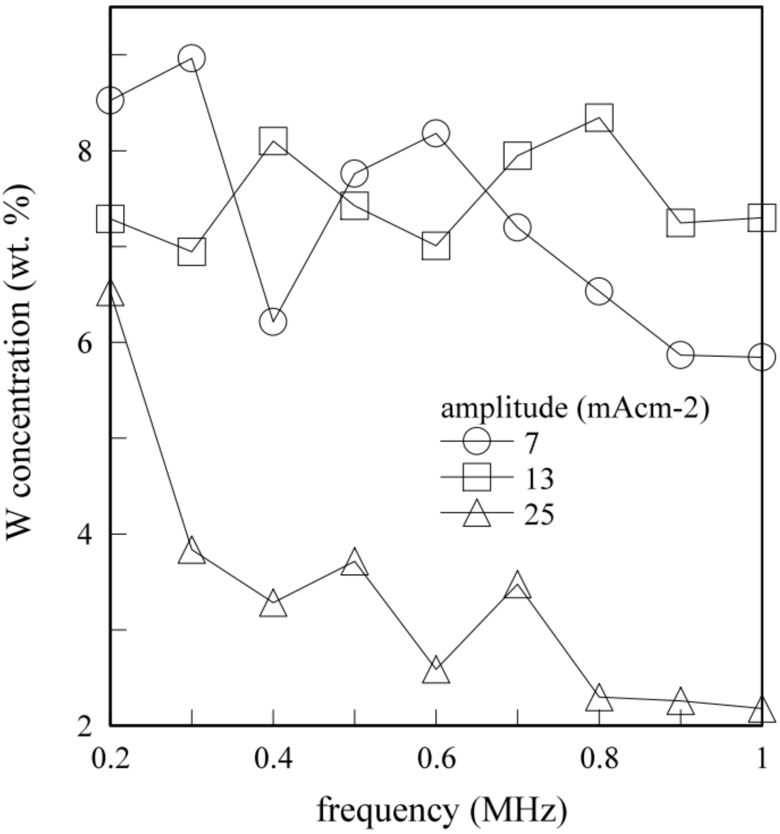

Figure 5. Frequency-dependence of the W concentration of the Cu-W thin film electrodeposited in the solution including 0.75 mol/L sodium tungstate dehydrate.

Figure 5 shows the dependence of the W concentration in the Cu-W thin film on the frequency. The W concentration periodically changes with the frequency as well as that in Fig. 2. The maximum W concentration is 9 wt. %, which is larger than 6 wt. % in Fig. 2. An increase in the concentration of sodium tungstate dehydrate simply causes the increase in the W concentration in the Cu-W film [26].

The W concentration dependent on the current density complicatedly behaves. The W concentration of the Cu-W thin film electrodeposited at 25 mA/cm^2 is smaller than that at 7 and 13 mA/cm^2 [27]. An increase in the current density lessens the W concentration in contrast with the dependence of the W concentration on the current density in Fig. 2. As the frequency increases, the W concentration in the Cu-W thin film electrodeposited at 7 mA/cm^2 is smaller or larger than that at 13 mA/cm^2. At the frequency beyond 0.7 MHz, the W concentrations in the Cu-W thin film electrodeposited at 7 mA/cm^2 are smaller than that at 13 mA/cm^2.

As stated the paragraph in Eq. (4), the transfer coefficient seems to change complicatedly. In addition, if several resonant frequencies at which the mass of Cu or W remarkably increases exist, the frequency dependence of the W concentration appears. As shown in Fig. 5, the W concentration in the Cu-W thin film changes with the frequency.

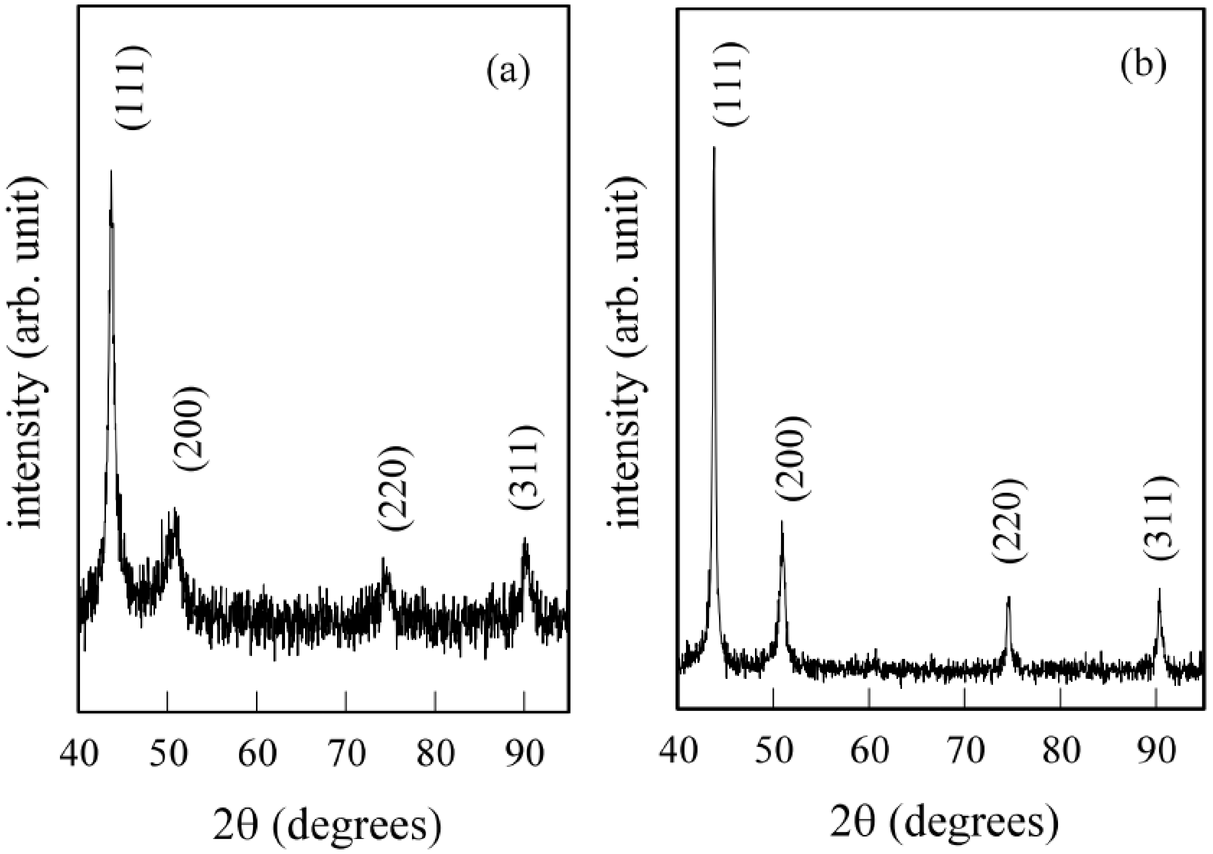

Figure 6. XRD charts of the Cu–W films electrodeposited in the solution including 0.75 mol/L sodium tungstate dehydrate (a) at an amplitude of 7 mA/cm^2 and a frequency of 0.3 MHz, and (b) at an amplitude of 25 mA/cm^2 and a frequency of 1 MHz. The Cu-W thin films of (a) and (b) had 4.6 μm and 4.3 μm in thickness.

Figure 6 shows XRD charts for two kinds of the Cu-W thin films that have a minimum W concentration at a current density of 7 mA/cm^2 and a maximum W concentration at a current density of 25 m A/cm^2. The diffraction peaks indexed as the (111), (200), (220), and (311) crystallographic planes are well consistent with those of polycrystalline copper [23] as well as those in Fig. 3. These diffraction peaks also indicate that the crystallographic planes parallel to the ITO glass exist in the Cu-W thin film. As no other diffraction peaks are observed, the Cu-Mo thin film is an alloy comprising Cu and W. Each diffraction peak in Fig. 6 is also broad in width. Using the Scherrer equation and [111] diffraction profile, the mean grain sizes of the Cu-W thin film in Figs. 6 (a) and (b) yield 12 nm and 21 nm. The mean grain size decreases with the W concentration. In other experiments reported previously [15, 28], the island diameter observed with SEM was an order of magnitude larger than the grain size calculated using the Scherrer equation, However, there was no explanation about the difference. The higher W concentration changes a poly-crystalline Cu-W thin film into an amorphous Cu-W thin film [24].

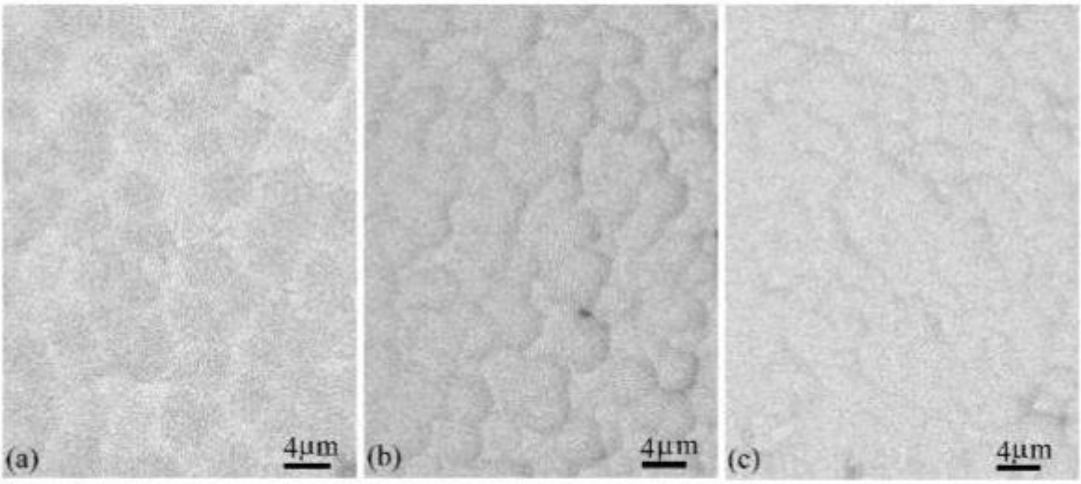

Figure 7. SEM images of the Cu-W films electrodeposited in the solution including 0.75 mol/L sodium tungstate dehydrate (a) at an amplitude of 7 mA/cm^2 and a frequency of 0.3 MHz, (b) at an amplitude of 13 mA/cm^2 and a frequency of 0.3 MHz, and (c) at an amplitude of 25 mA/cm^2 and a frequency of 1 MHz.

Figure 7 shows SEM images of the Cu-W films electrodeposited in the solution including 0.75 mol/L sodium tungstate dehydrate at (a) an amplitude of 0.7 mA/cm^2 and a frequency of 0.3 MHz, (b) an amplitude of 13 mA/cm^2 and a frequency of 1 MHz, and (c) an amplitude of 25 mA/cm^2 and a frequency of 1 MHz. All the Cu-W thin films comprise the island of which the surface appears the nano cauliflower as well as that in Fig. 4.

The size of the grain was reported to decrease with the W concentration [29]. The grain size in the Ni-W film including 13 wt. % became 63 nm. In light of the system different from that in our study, the value is approximately consistent with the grain size in this study.

4. CONCLUSIONS

The Cu-W thin film electrodeposited on the ITO glass substrate was found to be the alloy comprising Cu and W. The co-deposition of W and Cu was demonstrated using the solution that did not contain the iron group element. The maximum concentration of W in the Cu-W thin film became about 9 wt. %. The W concentration that changed with the frequency is explained by the energy level transition of electron. The SEM images of the Cu-W thin film showed that the surface morphology appeared as the nano-cauliflower.

References

1. A. Brenner, *Electrodeposition of Alloys*, Academic Press, New York, London, 1963.
2. N. Tsyntsaru, H. Cesiulis, M. Donten, J. Sort, E. Pellicer, and E. J. P-Murphy, *Surf. Eng. Appl. Electrochem.*, 48 (2102) 491.

3. N. Eliaz and E. Gileadi, *ECS Transactions*, 2 (2007) 337.
4. M. Saitou, K. Hamaguchi, and K. Inoue, *J. Phys. Chem. B*, 106 (2002)12253.
5. N. Sun, S. Lang, Y. Zhang, Y. Xu, H. Liu, and G. Li, *Fusion Energ.*, 35 (2016) 660.
6. K. Nitta, T. Nohira, R. Hagiwara, M. Majima, and S. Inazawa, *Electrochim. Acta*, 55 (2010) 1278.
7. M. Benaicha, M. Allam, A. Dakhouche, and M. Hamla, *Int. J. Electrochem. Sci.*, 11 (2016) 7605
8. N. Eliaz, T. M. Sridhar, and E. Gileadi, *Electrochim. Acta*, 50 (2005) 2893.
9. R. Juškėnas, I. Valsiūnas, V. Pakštas, A. Selskis,V. Jasulaitienė, V. Karpavičienė, V. Kapočius, *Appl. Surf. Sci.*, 253 (2006) 1435.
10. M. Zemanová, M. Krivosudská, M. Chovancová, and V. Jorík, *J. Appl. Electrochem.*, 41 (2011) 1077.
11. Q. Yang, Y. He1, Y. Fan, Y. Zhan, and Y. Tang, *Int. J. Electrochem. Sci.*, 11 (2016) 5103.
12. Z. A. Hamid, *Mater. Letters*, 57 (2003) 2558.
13. H. Capel, P.H. Shipway, and S.J. Harris, *Wear*, 255 (2003) 917.
14. M. Svensson, U. Wahlström, and G. Holmbom, *Surf. Coat. Technol*. 105 (1998) 218.
15. F-H. Su and P. Huang, *Mater. Chem. Phys.*, 134 (2012) 350.
16. P. Bacal, P. Indyka, Z. Stojek, and M. Donten, *Electrochem. Commun.*, 54 (2015) 28.
17. M. Saitou, *Int. J. Electrochem. Sci.*, 12 (2017) 1193.
18. M. Saitou, *Int. J. Electrochem. Sci.*, 11 (2016) 5535.
19. R. Guidelli, R. G. Compton, J. M. Feliu, E. Gileadi, J. Lipkowski, W. Schmickler, and S.Trasatti, *Pure Appl. Chem.*, 86 (2014) 245.
20. A. Yoshimori, T. Kakitani, and N. Mataga, *J. Phys. Chem.*, 93 (1989) 3694.
21. J-M. Saéant and D. Tessier, *Faraday Discuss. Chem. Soc.*, 74 (1982) 57.
22. M. Z. Bazant, *Acc, Chem. Res.*, 46 (2013) 1144.
23. JCPDS No. 04-0836.
24. P. Bacal, Z. Stojek, and M. Donten, *J. Solid State Electrochem.*, 20 (2016) 3143.
25. M. Xia, T. Lei, N. Lv, and N. Li, *Inter. J. Hydro. Ener.*, 39 (2014) 4794.
26. S. Costovicia, A-C. Maneab, T. Visanb, and L. Anicaia, *Electrochim. Acta*, 207 (2016) 97.
27. M. Gotou, T. Arakawa, N. Watanabe, T. Hara, T. Tomita, A. Hashimoto, H. Takanashi, and I. Koiwa, *Bull. Chem. Soc. Jpn.*, 2015, 88, 173,
28. N. Thangaraj, K. Tamilarsam, and D. Sasikumar, *Ind. J. Pure Appl. Phys.*, 52 (2014) 395.
29. M. H. Allahyarzadeh, M. Aliofkhazraei, A. R. Rezvanian, V. Torabinejad, and A. R. S. Rouhaghdam, *Surf. Coat. Technol.*, 307 (2016) 978.