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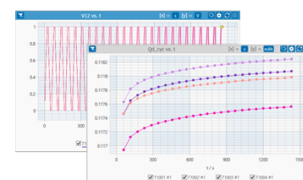
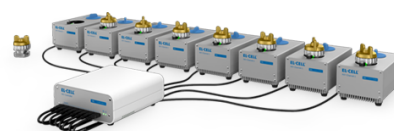
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Relationship between Oxygen Content and Crystal Structure of W Films Electrodeposited in Molten CsF–CsCl–WO₃

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The formation of W film with different crystal structures, α -W and β -W, has been reported in molten salt electroplating; however, the mechanism has not been sufficiently explored in previous studies. Here, the electrochemical behavior of W ions and the relationship between the oxygen content and crystal structure of electrodeposited W films were investigated in CsF–CsCl eutectic melts after adding 2.0 mol% of WO₃ at 773–973 K. The oxygen content in W films electrodeposited at various temperatures was analyzed using an inert gas fusion infrared absorption method. The oxygen content in the W films gradually decreased from 6.65 to 0.19 at% as the bath temperature increased from 773 to 973 K, and the crystal phase changed from β -W to α -W, as confirmed by X-ray diffractometry. Then, vacuum annealing treatment was performed on the β -W films electrodeposited at 823 K. Mirror-like α -W films were obtained after annealing at 973 K for 3 h; the oxygen content in the films decreased from 1.82 to 0.41 at%. This result shows that mirror-like α -W films are obtained by a two-step method of electrodeposition and vacuum annealing.

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Tungsten (W) metal is known for its refractory properties, including a high melting point, exceptional hardness, and remarkable heat resistance. It is anticipated to serve as a plasma-facing material in fusion reactors.¹ However, its hardness and brittleness make processing W into complex shapes challenging. Therefore, electrodeposition is considered an alternative method for preparing W materials due to the method's simple operation and low cost.

Tungsten has two distinct crystal structures: stable α -W with a bcc structure and metastable β -W with an A15 structure.² Recently, β -W has gained attention for its significant spin Hall effect and the largest spin Hall angle among transition metals,³ and is expected to be applied to spintronics.^{4,5} Previously, single-phase β -W films were primarily obtained using physical vapor deposition (PVD) methods, with the film thickness limited to the nanometer order.^{4–8}

Conversely, W electrodeposition has been investigated in several types of high-temperature molten salts: oxide molten salts,^{9–16} chloride molten salts,^{17–22} fluoride molten salts,^{23,24} and chloride-fluoride mixed molten salts.^{25–33} Among these reports, Takeda et al. gave a meticulous summary for previous study.³² While α -W has been successfully synthesized in various molten salts, only a few studies have reported the formation of β -W.^{19,20} We focused on CsF–CsCl molten salt due to its high-water solubility and low eutectic melting point (713 K, 50:50 mol%). Recently, we have reported that a mirror-like single-phase β -W film was obtained in molten CsF–CsCl–WO₃ at 773 K.³⁰ Additionally, we found that the crystal structure of electrodeposited W has temperature dependence, with β -W electrodeposited at 773 K and 823 K and α -W electrodeposited at 923 K.³¹ However, the mechanism of β -W formation by molten salt electrolysis remains underexplored and needs further investigation.

There are several reports on the mechanism of β -W formation when using the PVD method. Shen et al. obtained β -W by filling oxygen in a sputtering chamber using the PVD method, in which β -W films with a thickness of approximately 150 nm and oxygen content of 6–15 at% were formed.³⁴ Additionally, Chattaraj et al. used chemical molecular dynamics calculation to simulate the β -W structure and found that β -W became more stable than α -W thermodynamically with the inclusion of O, N, and F.³⁵ These reports suggest that the oxygen content in W films is a factor influencing the formation and stabilization of β -W. Therefore, the different crystal phases of the electrodeposited W films at varying

temperatures may be attributed to differences in oxygen content within the films.

The relationship between the crystal structure and oxygen content by preparing α -W and β -W films in molten CsF–CsCl–WO₃ at 773–973 K and analyzing the oxygen content in the electrodeposited W films. Furthermore, we investigate the crystal phase change of electrodeposited W films using annealing treatment to confirm the relationship between the crystal structure and oxygen content.

Experimental

Reagent grade CsF (>99.0%; Furuuchi Chemical Corp., Tokyo, Japan) and CsCl (>99.0%; FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) were dried in vacuum at 453 K for more than 24 h and at 773 K for 24 h. The salts were then mixed in a eutectic composition (CsF:CsCl = 50:50 mol%, 150 g), and the mixture was loaded in a glass-like carbon crucible (o.d.: 56 mm × i.d.: 53 mm × height 75 mm; Alliance Biosystems Inc., GAZ13-AB, Osaka, Japan). The crucible was placed at the bottom of a stainless-steel vessel. Subsequently, WO₃ (2.0 mol%) (99.9%; Kojundo Chemical Laboratory Co., Ltd., Tokyo, Japan) was directly added to the melt as the W(VI) ion source.

Electrochemical measurements and galvanostatic electrolysis were conducted in an Ar glove box (Pure Box System, ZYS16-0057, YAMATO Co., Ltd., Osaka, Japan), using a three-electrode method with an electrochemical measurement system (HZ-7000, Meiden Hokuto Corp., Tokyo, Japan). For the working electrodes, Cu foil (99.9%, thicknesses: 0.05 mm; Nilaco Corp., Tokyo, Japan), Ag flag (99.98%, diameter: 2.0 mm, thickness: 0.10 mm, Nilaco Corp., Tokyo, Japan), and Au flag (99.95%, diameter: 2.0 mm, thickness: 0.10 mm, Nilaco Corp., Tokyo, Japan) were selected. A glass-like carbon rod (diameter: 3.0 mm; Tokai Carbon Co., Ltd., Tokyo, Japan) was used as the counter electrode. A Pt wire (99.98%, diameter: 1.0 mm; Tanaka Precious Metal Technologies Co., Ltd., Tokyo, Japan) was employed as the quasi-reference electrode. The potential of the quasi-reference electrode was calibrated with respect to the dynamic Cs⁺/Cs potential determined by cyclic voltammetry performed on an Ag electrode. The melt temperature was measured using a type K thermocouple. The electrolyzed samples on the Cu foils were soaked in distilled water for 5 min at 333 K to remove the salt adhering to the deposits.

A mini lamp annealer (Advance Riko Inc., MILA-5050, Kanagawa, Japan) was used for vacuum annealing treatment of electrodeposited W samples. The samples were heated in vacuum using a turbo molecular pump (ULVAC Inc., YTP70A-D, Kanagawa, Japan).

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Phase identification of the W films was conducted using an X-ray diffractometer (XRD; Smart Lab, Cu-K α line, $\lambda = 1.5418$ Å, 40 kV, 40 mA; Rigaku Corp., Tokyo, Japan). A digital microscope (VHX-7100, KEYENCE Corp., Osaka, Japan) and a scanning electron microscope (SEM; Phenom Pro Generation 5, Thermo Fisher Scientific Inc., Waltham, MA) were employed for surface morphology observation. The oxygen content in the electrodeposited W films was analyzed using an inert gas fusion infrared absorption (IGF-IR) method (EMGA-930, Horiba Ltd., Kyoto, Japan).

Results and Discussion

Electrochemical behaviors of W ions.—Figure 1 shows the cyclic voltammograms on an Au flag electrode after the addition of WO₃ (2.0 mol%) in the molten CsF–CsCl at 773–973 K. The inset figure shows an enlarged view of around the start of the reduction currents. At 773 K (dark blue line), the cathodic current started to increase at around 1.42 V (vs Cs⁺/Cs), and then suddenly increased at around 1.37 V. It is assumed that W(VI) ions were first reduced to an intermediate product, and then further reduced to W metal. Similar behaviors were observed in our previous study.³⁰ At 823–923 K (light blue line, green line, and orange line), the two-step reduction behavior was also observed. However, at 973 K (purple line), the cathodic current suddenly increased at around 1.44 V, indicating the electrodeposition of W metal. At 973 K, it is thought that the intermediate product is not formed, or is immediately reduced to W metal. Therefore, the increase in temperature might affect the formation of the intermediate product during W electrodeposition.

In addition, the cathodic peak currents increased with increasing temperature. We have reported the solubility of WO₃ in molten CsF–CsCl at different temperatures, which is determined to be 1.0 mol%, 1.4 mol%, 3.1 mol%, and 4.9 mol% at 773 K, 823 K, 873 K, 923 K, and 973 K, respectively.³¹ In the present study, the amount of added WO₃ was set as 2.0 mol%. According to the solubility of WO₃, only part of the WO₃ was dissolved in the melt at 773 K and

823 K. When the temperature was increased to 873 K, all of the WO₃ dissolved, leading to the large increase in the cathodic peak current compared to that at 823 K. At 923 K and 973 K, the cathodic peak current increased slightly, which is explained by the higher diffusion rate of W ions at higher temperatures.

Electrodeposition of W films.—*Surface morphology and current efficiency.*—Samples were prepared by galvanostatic electrolysis of Cu plate electrodes at a current density of 6 mA cm^{−2} at 773–973 K. Optical and SEM images of the samples obtained at various temperatures are exhibited in Fig. 2. Metallic luster was observed on the samples obtained at 773 K, 823 K, and 873 K, while gray and black surfaces were observed on the samples obtained at 923 K and 973 K. In particular, the films obtained at 773 K and 823 K have a mirror-like surface, indicating a high smoothness of the surface.

In the SEM images, for the samples obtained at 773 K and 823 K, crystal grains could hardly be observed. For the sample obtained at 873 K, small spherical grains were observed on the entire surface of the samples. The sample obtained at 923 K exhibited a surface with angular crystal grains. As for the sample obtained at 973 K, an inhomogeneous surface with gaps was observed, indicating that a rough-surfaced film was obtained. The surface morphology of electrodeposits is temperature-dependent, with smoother surfaces more easily obtained at lower temperatures.

To calculate the current efficiency, the mass change (m_{gain}) was calculated by measuring the mass of the Cu substrate before electrodeposition (m_{bef}) and the total mass after electrodeposition (m_{aft}). The current efficiency (η) was calculated, assuming a 6-electron reaction from W(VI) to W(0), using the following formula:

$$\eta = (6 \cdot F \cdot m_{\text{gain}}) / (S \cdot q \cdot M_{\text{W}}) \times 100\% \quad [1]$$

where F is the Faraday constant, S is the electrode area (1.015 cm²), q is the charge density (90 C cm^{−2}), and M_{W} is the molar weight of W. The calculation results are listed in Table I. Samples obtained at

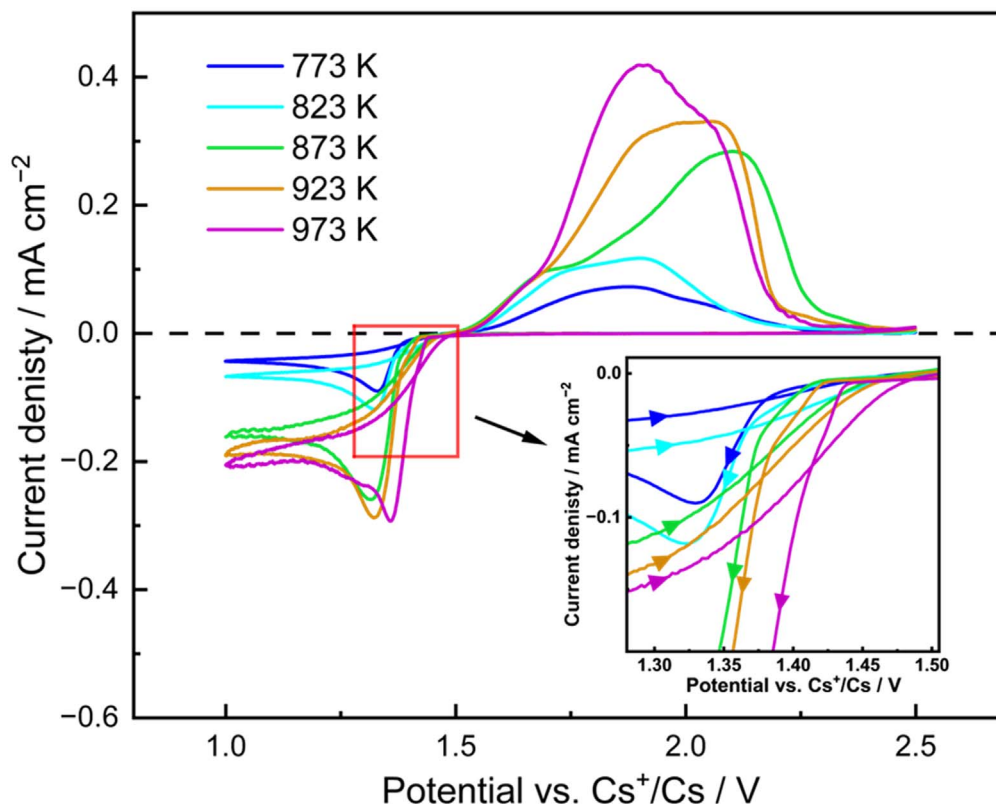


Figure 1. Cyclic voltammograms of an Au flag electrode in molten CsF–CsCl salt after addition of WO₃ (2.0 mol%) at 773–973 K. Inset figure shows an enlarged view of around the start of the reduction currents. Scan rate: 0.2 V s^{−1}.

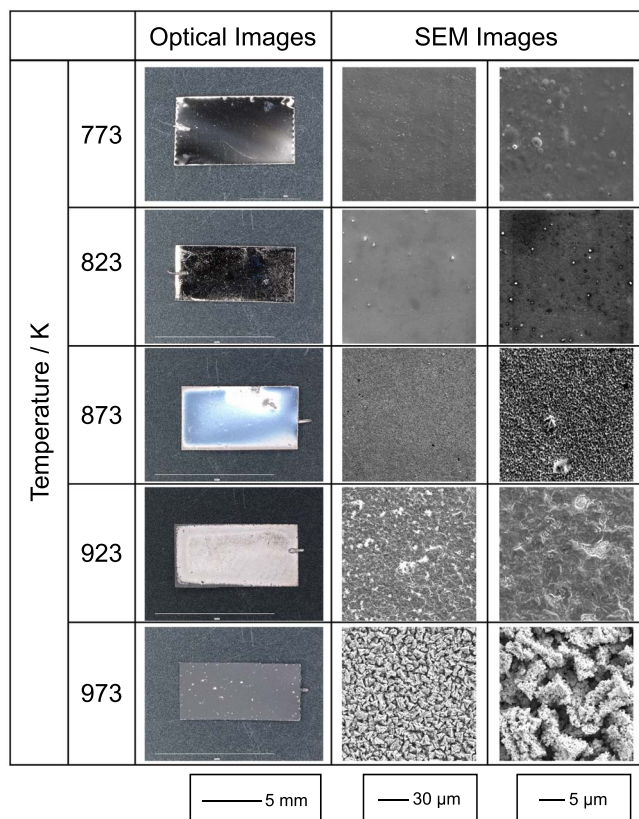


Figure 2. Optical and SEM images of the samples obtained by galvanostatic electrolysis of Cu plate electrodes with a current density of 6 mA cm^{-2} in molten CsF-CsCl-WO_3 (2.0 mol% added) at 773–973 K. Charge density: 90 C cm^{-2} .

773 K exhibited an average current efficiency of 63.5%. W deposition is predicted to be a multi-step process; W(VI) ions are reduced to intermediate products, such as W(IV) ions or W(II) ions, and then furtherly reduced to W metal. As for W deposition at 773 K, only a part of the W intermediate product was reduced to W metal, while the rest might diffuse to the bulk, resulting in the loss of current efficiency. Samples obtained at 823 K, 873 K, and 923 K exhibited high average current efficiencies of over 80%; this is explained by the increase in reduction ratio of W intermediate products to W metal as the temperature increases. The average current efficiency of the samples obtained at 973 K was 68.9%; this is believed to result from reduced adhesion due to the formation of surface irregularities and the shedding of some of the deposits during electrolysis.

Relationship between crystal structure and oxygen content.—XRD patterns of the samples are illustrated in Fig. 3. All XRD patterns were identified with either α -W or β -W. Only β -W was

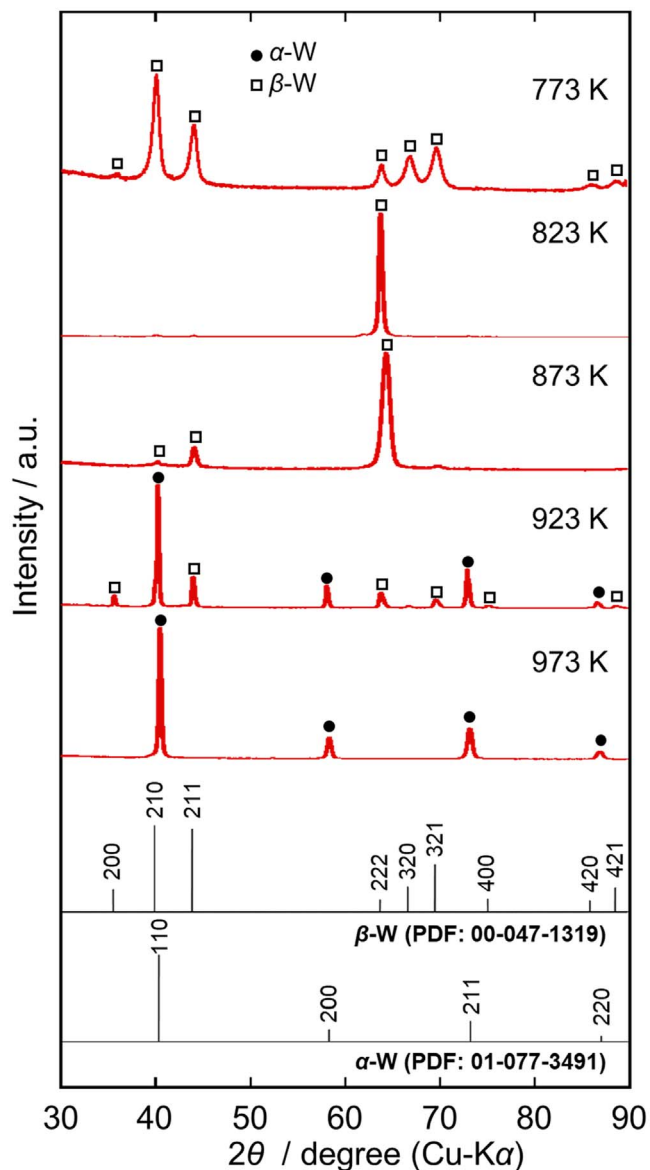


Figure 3. XRD patterns of the samples obtained by galvanostatic electrolysis of a Cu plate electrode with a current density of 6 mA cm^{-2} in molten CsF-CsCl-WO_3 (2.0 mol% added) at 773–973 K. Charge density: 90 C cm^{-2} .

detected at temperatures of 773 K, 823 K, and 873 K. The β -W films obtained at 823 K and 873 K were strongly oriented along the {111} plane, which had also been reported in our previous study.³¹ A mixture of α -W and β -W was detected at 923 K, while only α -W was detected at 973 K. In our previous study, a mixture of α -W and β -W was obtained in molten CsF-CsCl-WO_3 at 873 K.³¹ A slight difference was found in the temperature at which the mixture of α -W and β -W was obtained. This is thought to be due to the different amount of added WO_3 : 1.0 mol% WO_3 was added in the previous study, whereas 2.0 mol% was added in the present study.

Subsequently, the oxygen contents in the electrodeposited W films were investigated by an IGF-IR method. 0.5 g of Sn and 0.5 g of Ni were used as solvents to help with the combustion of W films. The combustion period lasted for 75 s with an input power of 5.50 kWh. As illustrated in Fig. 4, the oxygen contents in the W films gradually decreased from $6.65 \pm 0.11 \text{ at}\%$ to $0.19 \pm 0.10 \text{ at}\%$ as the bath temperature increased from 773 K to 923 K. As mentioned above, the crystal structure of electrodeposited W changed from β -W to α -W as the bath temperature increased. These results suggest

Table I. Current efficiency in the electrodeposition of W on Cu plate electrodes in molten CsF-CsCl-WO_3 (2.0 mol% added) at various temperatures.

Temperature T/K	Number of samples n	Current efficiency ^{a,b} $\eta/\%$
773	5	63.5 ± 9.5
823	9	90.6 ± 1.5
873	5	83.4 ± 3.0
923	5	82.3 ± 4.0
973	5	68.9 ± 7.1

a) Average value ($\pm$ standard error) calculated under the 6-electron reaction for W deposition. b) $\eta = \frac{6 \cdot F \cdot m_{\text{gain}}}{S \cdot q \cdot M_{\text{W}}} \cdot 100$, $M_{\text{W}} = 183.84 \text{ g mol}^{-1}$, $S = 1.015 \text{ cm}^2$, $m_{\text{gain}} = m_{\text{aft}} - m_{\text{bef}}$.

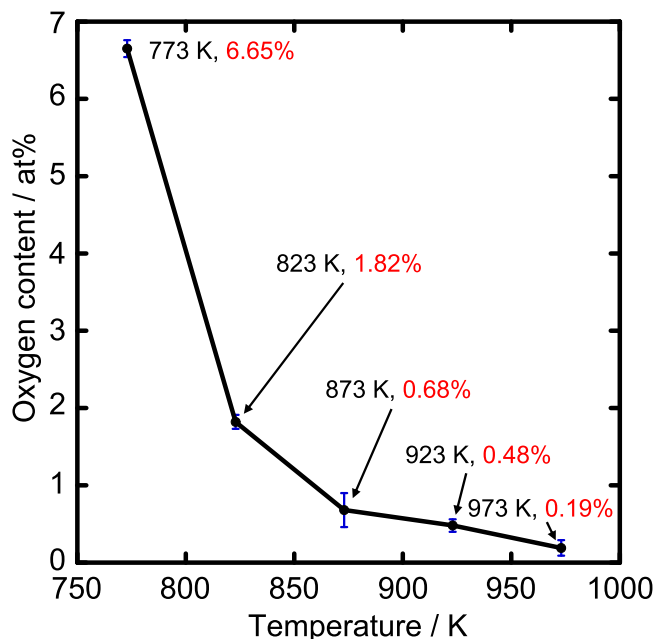
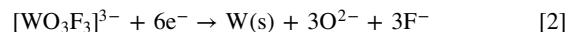


Figure 4. Oxygen contents of the samples obtained by galvanostatic electrolysis of a Cu plate electrode with a current density of 6 mA cm^{-2} in molten CsF-CsCl-WO_3 (2.0 mol% added) at 773–973 K. Charge density: 90 C cm^{-2} . Error bars represent the standard error of the mean, $n = 3$.

that the presence of oxygen in W films stabilizes β -W. Although the position of the oxygen atoms in the β -W has not yet been fully clarified, Arita et al. calculated the XRD patterns of $(\text{W}_3\text{W})\text{O}_x$, in which the oxygen atoms occupy interstitial sites, and ordered W_3O , in which the oxygen atoms occupy substitutional sites, in order to elucidate the position of the oxygen atoms in β -W(A15). The former gave the same XRD pattern as pure β -W (A15), and the latter gave the 110, 220, and 310 diffraction lines in addition to the XRD pattern of β -W (A15).³⁶ Since the same XRD pattern as pure β -W metal was obtained in the present study, the oxygen is thought to occupy the interstitial sites. Also, Sluiter reported that C, N, O, and F cannot dissolve substitutionally in β -W according to the results of ab initio calculation,³⁷ which is consistent with our opinion.

Furthermore, our group had reported that the structure of the W(VI) ions in CsF-CsCl-WO_3 is $\text{fac-}[\text{WO}_3\text{F}_3]^{3-}$ by Raman Spectroscopy.³¹ Thus, the total reaction of the reduction of W ions during electrolysis can be described by the following formula:



It is believed that covalent W–O bonds in $[\text{WO}_3\text{F}_3]^{3-}$ partially remained during the reduction, which led to the inclusion of oxygen in β -W films. However, a higher temperature provides abundant energy to promote the dissociation of covalent W–O bonds, leading to the lower oxygen content in electrodeposited W films and the formation of α -W.

Annealing treatment of electrodeposited β -W.—*Surface morphology.*—To further confirm the relationship between the crystal structure and oxygen content in W films, vacuum annealing treatment was conducted using β -W films electrodeposited at 823 K. The samples were heated to 973 K in 10 min under vacuum conditions ($3 \times 10^{-3} \text{ Pa}$) and then held for 3 h. Figure 5 illustrates the optical and SEM images of as-electrodeposited β -W obtained at 823 K and after annealing at 973 K. After annealing at 973 K, metallic luster can still be observed, and almost no change occurs in surface morphology.

Relationship between crystal structure and oxygen content.—The XRD analysis results of the samples before and after annealing treatment are illustrated in Fig. 6. Electrodeposited β -W films were transformed to pure α -W after annealing at 973 K. As previously introduced in this study, α -W films electrodeposited at 973 K showed a rough and uneven surface. Conversely, α -W films fabricated by annealing treatment using electrodeposited β -W films are dense and possess a mirror-like surface. Therefore, we provide a promising method for preparing smooth and dense α -W films, which is inexpensive and easy to operate compared to traditional W processing methods, such as mechanical polishing.

Furthermore, the oxygen content of the β -W films annealed at 973 K was analyzed by an IGH-IR method. The oxygen content in the W film decreased from $1.82 \pm 0.09 \text{ at\%}$ to $0.41 \pm 0.21 \text{ at\%}$ after vacuum annealing treatment, accompanied by crystal phase change from β -W to α -W. Shen and Mai prepared thin β -W films using the PVD method and found out that β -W films became unstable at high temperatures and changed to α -W under vacuum above 900 K.³⁴ In

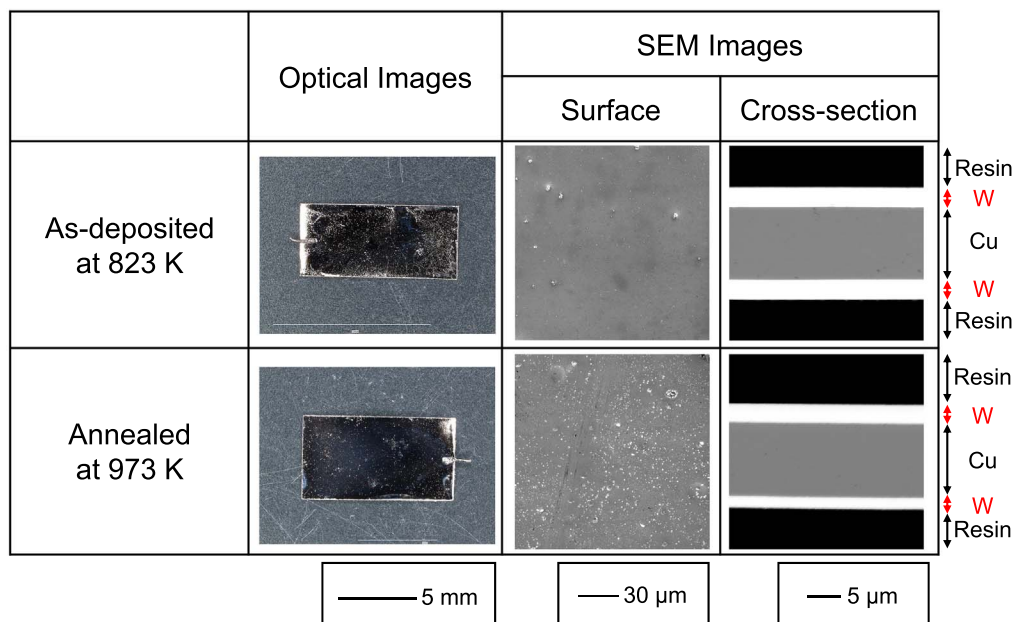


Figure 5. Optical and SEM images of the β -W films as-electrodeposited at 823 K and after annealing at 973 K for 3 h.

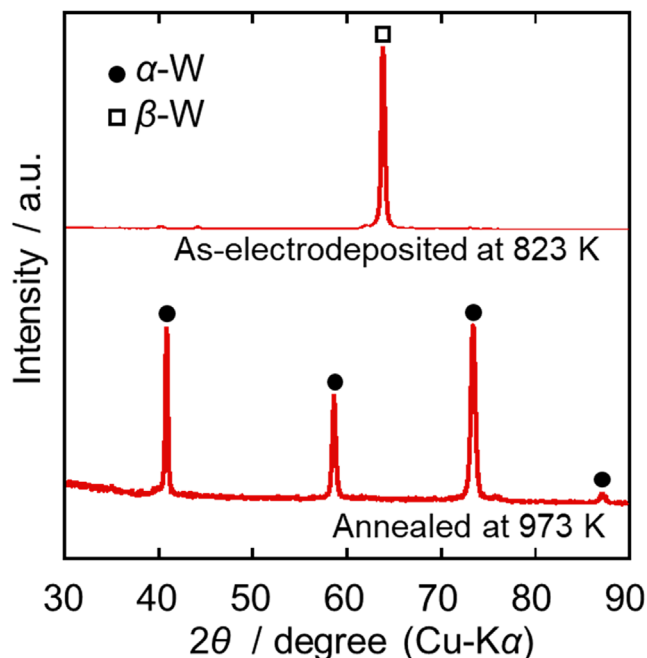


Figure 6. XRD patterns of the β -W films as-electrodeposited at 823 K and after annealing at 973 K for 3 h.

addition, Chattaraj et al. claimed that ab initio calculations show a higher solution energy of oxygen in β -W and a tendency to transform locally from α to β phase with increasing oxygen concentration.³⁵ Therefore, in this study, the reason for the phase transformation from β -W to α -W is speculated to be the breaking down of covalent W–O bonds in β -W, resulting in the removal of oxygen. Here, the oxygen partial pressures in equilibrium with WO_2 and WO_3 at 900 K are calculated to be 2.2×10^{-20} Pa and 3.8×10^{-31} Pa, respectively, from the Gibbs energies of formation.³⁸ These values are much lower than the pressure during the annealing process, suggesting that these tungsten oxides are stable and no release of oxygen gas occurs. Cantalini et al. reported the fabrication of WO_3 film by evaporation of WO_3 under 1.0×10^{-3} Pa at 783 K.³⁹ In the present study, annealing treatment was conducted under 3.0×10^{-3} Pa at 973 K. Therefore, the oxygen in W films was speculated to be removed as WO_3 gas during the annealing treatment process.

Conclusions

The relationship between the oxygen content and crystal structure of electrodeposited W films was investigated. Cyclic voltammetry was carried out in molten CsF – CsCl – WO_3 (2.0 mol% added) at 773–973 K. The results suggested the formation of an intermediate product before the electrodeposition of W metal at 773–923 K, but not at 973 K. W films electrodeposited in molten CsF – CsCl – WO_3 (2.0 mol% added) at various temperatures showed different crystal phases; the β -W phase was obtained at 773–873 K, the mixture of α -W and β -W phase was obtained at 923 K, and the α -W phase was obtained at 973 K. As the temperature increased, the oxygen content gradually decreased from 6.65 at% to 0.19 at%, accompanied by the crystal phase change from β -W to α -W. Single-phase β -W electrodeposited at 823 K transformed into α -W after vacuum annealing at 973 K, and the oxygen content decreased from 1.82 at% to 0.41 at%. The phase transformation from β -W to α -W was believed to occur due to the breakdown of covalent W–O bonds in β -W, leading to the

release of oxygen as WO_3 . Furthermore, α -W films obtained by vacuum annealing have a mirror-like surface, indicating that the two-step method of electrodeposition and vacuum annealing is useful for preparing the α -W films with smooth surfaces.

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References

1. T. Hirai et al., *Nuclear Materials and Energy*, **9**, 616 (2016).
2. H. Hartmann, F. Ebert, and O. Bretschneider, *Z. Anorg. Allg. Chem.*, **198**, 116 (1931).
3. Q. Hao and G. Xiao, *Phys. Rev. Appl.*, **3**, 034009 (2015).
4. Q. Hao, W. Chen, and G. Xiao, *Appl. Phys. Lett.*, **106**, 182403 (2015).
5. C.-F. Pai, L. Liu, Y. Li, H. W. Tseng, D. C. Ralph, and R. A. Buhrman, *Appl. Phys. Lett.*, **101**, 122404 (2012).
6. M. Rossnagel, I. C. Noyan, and C. Cabral, *J. Vac. Sci. Technol. B*, **20**, 2047 (2002).
7. D. Choi et al., *J. Vac. Sci. Technol. A*, **29**, 051512 (2011).
8. S. Lee, J. Cho, and C.-Y. You, *J. Vac. Sci. Technol. A*, **34**, 021502 (2016).
9. Y. H. Liu, Y. C. Zhang, Q. Z. Liu, X. L. Li, and F. Jiang, *Fusion Eng. Des.*, **87**, 1861 (2016).
10. Y. Liu, Y. Zhang, F. Jiang, B. Fu, and N. Sun, *J. Nucl. Mater.*, **442**, S585 (2013).
11. N. Sun, Y. Zhang, F. Jiang, S. Lang, and M. Xia, *Fusion Eng. Des.*, **89**, 2529 (2014).
12. F. Jiang, Y. Zhang, N. Sun, and J. Leng, *Appl. Surf. Sci.*, **327**, 432 (2015).
13. F. Jiang, Y. Zhang, N. Sun, W. Cheng, and X. Ding, *J. Nucl. Mater.*, **455**, 416 (2014).
14. F. Jiang, Y. Zhang, N. Sun, and Z. Liu, *Appl. Surf. Sci.*, **317**, 867 (2014).
15. F. Jiang, Y. Zhang, N. Sun, and J. Len, *Appl. Surf. Sci.*, **331**, 278 (2015).
16. W. Qin, X. Xi, L. Zhang, Z. Nie, C. Liu, and R. Li, *J. Electroanal. Chem.*, **935**, 117314 (2023).
17. P. G. Dudley, D. Inman, and S. H. White, *Proc. Second International Symposium on Molten Salts, The Electrochemical Society*, **29**, (1981).
18. D. Zuckerbrot and R. A. Bailey, *Proc. Fourth International Symposium on Molten Salts, The Electrochemical Society*, **571**, (1984).
19. A. Katagiri, M. Suzuki, and Z. Takehara, *J. Electrochem. Soc.*, **138**, 767 (1991).
20. H. Takenishi and A. Katagiri, *Electrochemistry*, **67**, 669 (1999).
21. M. Masuda, H. Takenishi, and A. Katagiri, *J. Electrochem. Soc.*, **148**, C59 (2001).
22. H. Nakajima, T. Nohira, and R. Hagiwara, *Electrochem. Solid-State Lett.*, **8**, C91 (2005).
23. S. Senderoff and G. W. Mellors, *Science*, **153**, 3743 (1966).
24. S. Senderoff and G. W. Mellors, *J. Electrochem. Soc.*, **114**, 586 (1967).
25. H. Nakajima, T. Nohira, R. Hagiwara, K. Nitta, S. Inazawa, and K. Okada, *Electrochim. Acta*, **53**, 24 (2007).
26. K. Nitta, M. Majima, S. Inazawa, T. Nohira, and R. Hagiwara, *Electrochemistry*, **77**, 621 (2009).
27. K. Nitta, T. Nohira, R. Hagiwara, M. Majima, and S. Inazawa, *Electrochim. Acta*, **55**, 1278 (2010).
28. T. Nohira, K. Kitagawa, R. Hagiwara, K. Nitta, M. Majima, and S. Inazawa, *Trans. Mater. Res. Soc. Jpn.*, **35**, 35 (2010).
29. T. Nohira, T. Ide, X. Meng, Y. Norikawa, and K. Yasuda, *J. Electrochem. Soc.*, **168**, 046505 (2021).
30. X. Meng, Y. Norikawa, and T. Nohira, *Electrochem. Commun.*, **132**, 107139 (2021).
31. Y. Norikawa, X. Meng, K. Yasuda, and T. Nohira, *J. Electrochem. Soc.*, **169**, 102506 (2022).
32. O. Takeda, S. Watanabe, C. Iseki, X. Lu, and H. Zhu, *J. Electrochem. Soc.*, **169**, 122503 (2022).
33. Y. Norikawa and T. Nohira, *Acc. Chem. Res.*, **56**, 1698 (2023).
34. Y. G. Shen and Y. W. Mai, *Mater. Sci. Eng.*, **28**, 176 (2000).
35. A. Chattaraj et al., *Sci. Rep.*, **10**, 14718 (2020).
36. M. Arita and I. Nishida, *Jpn. J. Appl. Phys.*, **32**, 1759 (1993).
37. M. H. F. Sluiter, *Phys. Rev. B*, **80**, 22 (2009).
38. I. Barin, *Thermochemical Data of Pure Substance* (VCH Verlagsgesellschaft, Weinheim) 3rd ed. (1995).
39. C. Cantalini, H. T. Sun, M. Faccio, M. Pelino, S. Santucci, L. Lozzi, and M. Passacantando, *Sens. Actua. B: Chem.*, **31**, 81 (1996).