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Abrasive-free polishing of tungsten alloy using electrochemical etching

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ABSTRACT

Tungsten alloy is a crucial engineering material for electrical and optical applications. However, damage-free and highly efficient polishing of tungsten has not been realized yet. We report the abrasive-free polishing of tungsten alloy using electrochemical polishing (ECP), which is an etching process. To achieve balance between polishing efficiency and surface quality, a two-step ECP process has been proposed. Current-driven ECP lasting for 3 min, as the first step, quickly removed the surface grinding marks and subsurface damage while the following potential-driven ECP lasted for 20 min, as the second step, improved the surface roughness and an ultra-smooth surface with an Ra roughness of 17.6 nm was finally obtained.

1. Introduction

Tungsten, as a transition and refractory metal, has been used in various fields owing to its excellent physical, mechanical and chemical properties. Tungsten is widely used as the wiring material in fabrication of integrated circuits owing to its good electric conductivity and low coefficient of thermal expansion [1,2]. Tungsten has also been used in some high temperature applications such as SEM filaments or nozzles for high temperature fluids owing to its high melting point (3422 ± 15 °C), which is the highest of all metals [3,4].

In recent years, glass molding, which is a newly emerging but promising application of tungsten, has been proposed [5]. Currently, most optical glass lenses are produced by molding using ultra-precision molds made of sintered tungsten carbide (WC) [6,7] or chemical vapor deposition-silicon carbide (CVD-SiC) [8,9]. WC and SiC have many excellent chemical and mechanical properties, like strong chemical inertness, high oxidation temperature, low coefficients of thermal expansion, high hot hardness and so on, making them superior as the mold materials for precision molding of glass lenses. However, these hard and brittle materials are difficult to machine using conventional ultra-precision machining methods like cutting, grinding and polishing [10]. These problems in machining of WC and SiC greatly limit the cost-reduction of the molding process. Thus, in recent years, tungsten alloy has been proposed to be used as the mold insert material for replacement of WC or SiC. Tungsten has lower hardness than WC and SiC but is hard enough for glass molding. Meanwhile, tungsten has better thermal properties such as a high melting temperature and a low coefficient thermal expansion. More importantly, tungsten alloy is machinable using commercial carbide tools. These properties make tungsten a very economic mold material for glass molding.

For removal of subsurface damage and improvement of surface roughness, polishing is an indispensable step in the manufacturing process of tungsten alloy molds. Chemical mechanical polishing (CMP) using silica slurry has been widely used to polish tungsten substrates [11,12]. Even though excellent polishing characteristics of CMP have been demonstrated, the low polishing efficiency and large amount consumption of slurry make it a costly process. A highly efficient and slurry-free polishing technique, electrochemical polishing (ECP), has been widely used for planarization or polishing of metals or semiconductor substrates [13]. ECP is more cost-effective than CMP as there is no need to use slurry. Meanwhile, it is a damage-free process as there is no mechanical removal in ECP [14]. Recently, ECP has been applied to polish some difficult-to-polish metal materials like titanium alloy [15].

In this communication, an abrasive-free and highly efficient polishing process based on electrochemical etching is applied to tungsten alloy and the results are presented.

2. Experimental

2.1. Electrochemical polishing (ECP) of tungsten

The substrates used in this research are pure tungsten alloy (> 99.99%) with a diameter of 8 mm. The substrates were cut from a tungsten rod using electro-discharge machining and their end faces were ground using a diamond grinding wheel (#120). Fig. 1 shows the

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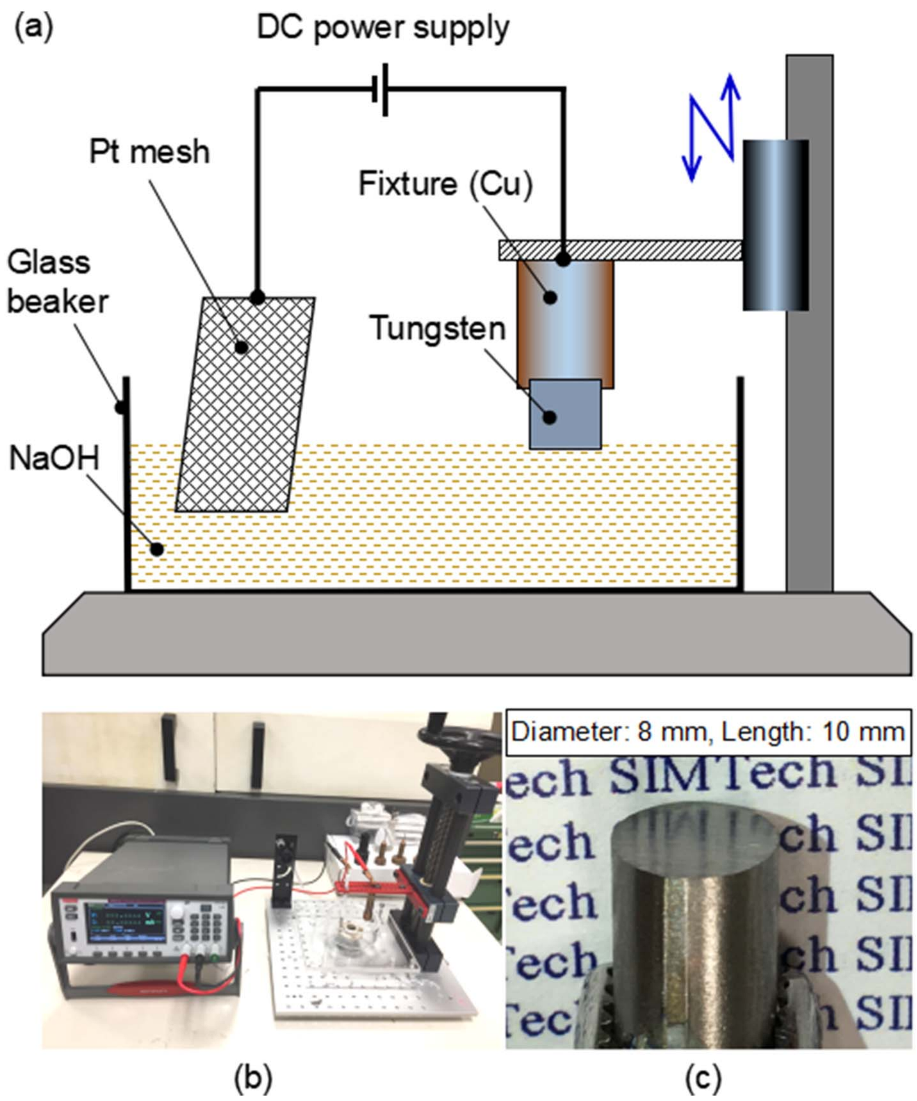


Fig. 1. Schematic (a) and photo (b) of experimental setup and photo (c) of tungsten substrate.

schematic and photo of experimental setup used in this work. Etching was performed in a glass beaker and NaOH solution was used as the electrolyte. A platinum mesh (20 mm × 20 mm) was used as the counter electrode and tungsten substrate as the working electrode. KEITHLEY 2280S provided electric current to perform electrochemical etching. To realize electric contact, the tungsten substrate was inserted into a copper fixture which was mounted on a vertical lifting platform. The distance between the substrate center and the counter electrode was 30 mm. During anodizing, the position of the substrate was manually adjusted to ensure that only the downward end face was immersed in the electrolyte and etched. After anodic etching, samples were rinsed in water and dried by blowing N_2.

ECP of tungsten, which is an electrochemical etching process, is based on the simultaneous anodic oxidation and dissolution. The electrochemical reactions occurring on the cathode (platinum mesh) and anode (tungsten) can be expressed as follows:

Cathode:

$$6H_2O + 6e^- \rightarrow 3H_2\ (g) + 6OH^- \tag{1}$$

Anode:

$$W\ (s) + 6OH^- \rightarrow WO_3\ (s) + 3H_2O + 6e^- \tag{2}$$

$$WO_3\ (s) + 2OH^- \rightarrow WO_4{}^{2-} + H_2O \tag{3}$$

Anodizing as Eq. (2) occurs on the surface of tungsten and tungsten is oxidized to WO_3. The generated WO_3 reacts with the electrolyte (NaOH) and gets dissolved as Eq. (3). The flattening mechanism of ECP has been widely studied and several hypotheses have been proposed among which “viscous film theory” proposed by Jacquet is most widely accepted [16]. According to the viscous film theory, the dissolution products accumulate near the anode and form a viscous layer that increases the electrical resistance of the system and limits the current. This viscous layer over peaks is much thinner than over depressions. Consequently, the electric current density over peaks of substrate surface is higher than that over depressions, which results in the fact that peaks dissolved faster and the leveling effect can be expected.

2.2. Characterization

The loose weights of tungsten substrates were measured to calculate the material removal rate (MRR) of ECP. Before and after ECP, the surface roughness was confirmed by measurements using a stylus profilometer (Talysurf 200) while the surface morphology was measured by a scanning electron microscopy (SEM, Hitachi S-4800). Surface composition of tungsten substrates before and after polishing was measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi), in which AlKa (1486.6 eV) radiation served as the excitation source and the measuring area was 900 μm in diameter.

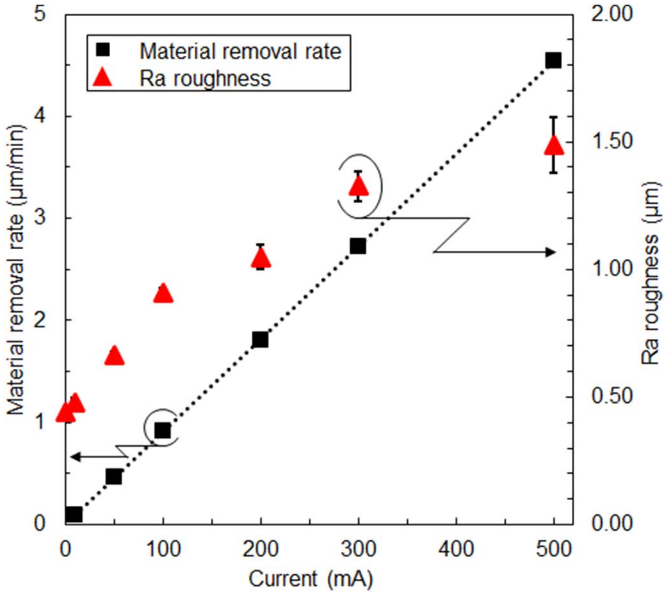


Fig. 2. Variation of MRR and Ra roughness in current-driven ECP.

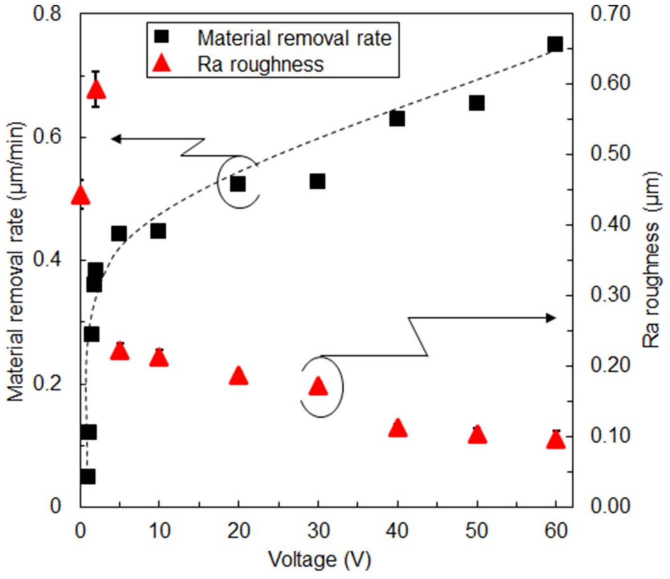


Fig. 3. Variation of MRR and Ra roughness in potential-driven ECP.

3. Results and discussion

As an electrochemical etching process, there are two polishing modes in ECP: the current-driven ECP mode which works under the high current and low potential condition and the potential-driven ECP mode which works under the low current but high potential condition. The switching between these two ECP modes can be realized by changing the electrolyte conductivity. In order to evaluate the polishing performance of these two ECP modes, MRRs and surface roughness of current-driven ECP and potential-driven ECP were investigated.

Current-driven ECP using 5.0 wt% NaOH solution (Electric conductivity: 206 mS/cm) as the electrolyte was conducted on tungsten substrates ground by diamond wheels. In each ECP experiment, the polishing duration was 10 min. Fig. 2 shows the variation of MRR and mean roughness (Ra) value (measuring length: 5 mm) in current-driven ECP with different current values. It was found that the MRR linearly increases with the increasing of the current, demonstrating that electrolysis of water does not occur in the ECP process. When the current was 500 mA, a high MRR of about 4.5 μm/min, which was much higher than that of conventional CMP processes [11], was achieved. However, it was also found that the roughness value (Ra) of the polished surface deteriorated in current-driven ECP. With a constant current of 500 mA, the Ra roughness of the polished surface was about 1.5 μm, which is much rougher than the original surface. The results shown in Fig. 2 reveal that current-driven ECP can realize highly efficient polishing of tungsten though no flattening effect has been demonstrated.

For comparison, potential-driven ECP using 1.0 wt% NaOH solution (electric conductivity: 48.6 mS/cm) as the electrolyte was also conducted. Fig. 3 shows the variation of MRR and Ra roughness values (measuring length: 5 mm) in potential-driven ECP with different potential values. It can be found that after the potential exceeds the standard oxidation potential (SOP), the MRR only slightly increases with the increasing of the potential. When the potential was 60 V, the MRR was only 0.75 μm/min, which was much lower than that of ECP under the current-driven mode. However, it was also found that the Ra roughness of the polished surface has been drastically improved after potential-driven ECP. When the potential was 60 V, the surface Ra roughness has decreased from 0.44 μm (as-ground surface) to below 0.10 μm. The results shown in Fig. 3 reveal that potential-driven ECP can realize a smooth tungsten surface though its polishing efficiency is relatively lower.

A probable mechanism was proposed to explain the results shown in Figs. 2 and 3. The thickness of viscous layer formed in ECP depends on the dissolution rate which is determined by the current value. In current-driven mode, the relatively high current value results in a relatively thick viscous layer. As the potential is low and the viscous layer is thick, the differentiation of the strength of electric field distributed in the viscous layer, which determines the flattening effect of ECP [16], is small. Thus, according to the viscous layer theory, surface flattening by preferential removal of the protruding areas, around which the electric field is centralized, will not occur. On the other hand, in potential-driven mode, the differentiation of the strength of electric field distributed in the thin viscous layer is much larger and an excellent flattening effect has been demonstrated. This mechanism can explain why the surface roughness greatly deteriorated during current-driven ECP but was drastically improved in potential-driven ECP.

To achieve the balance between polishing efficiency and surface quality, a two-step ECP processing was developed. In the first step, current-driven ECP was conducted for large volume material removal (rough polishing). Then, in the second step, potential-driven ECP was conducted for surface finishing (fine polishing). Fig. 4 shows the voltage and current curves of the proposed two-step ECP process with the electrolyte replacement interval which lasted for about 5 min ignored. In the current-driven step, the current was set to 500 mA and the duration was 3 min. 5 wt% NaOH solution was used as the electrolyte. According to Fig. 2, the MRR was 4.5 μm/min, meaning that the surface

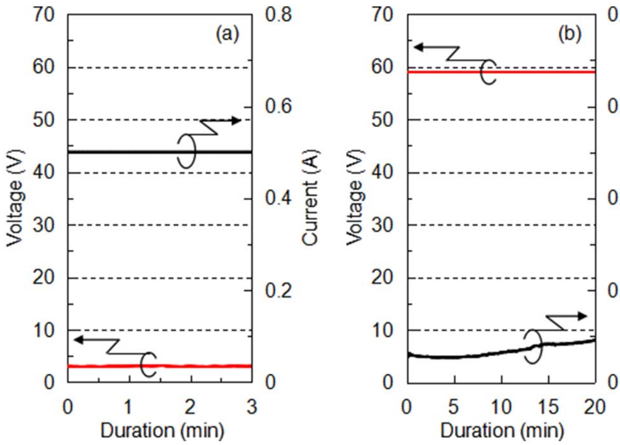
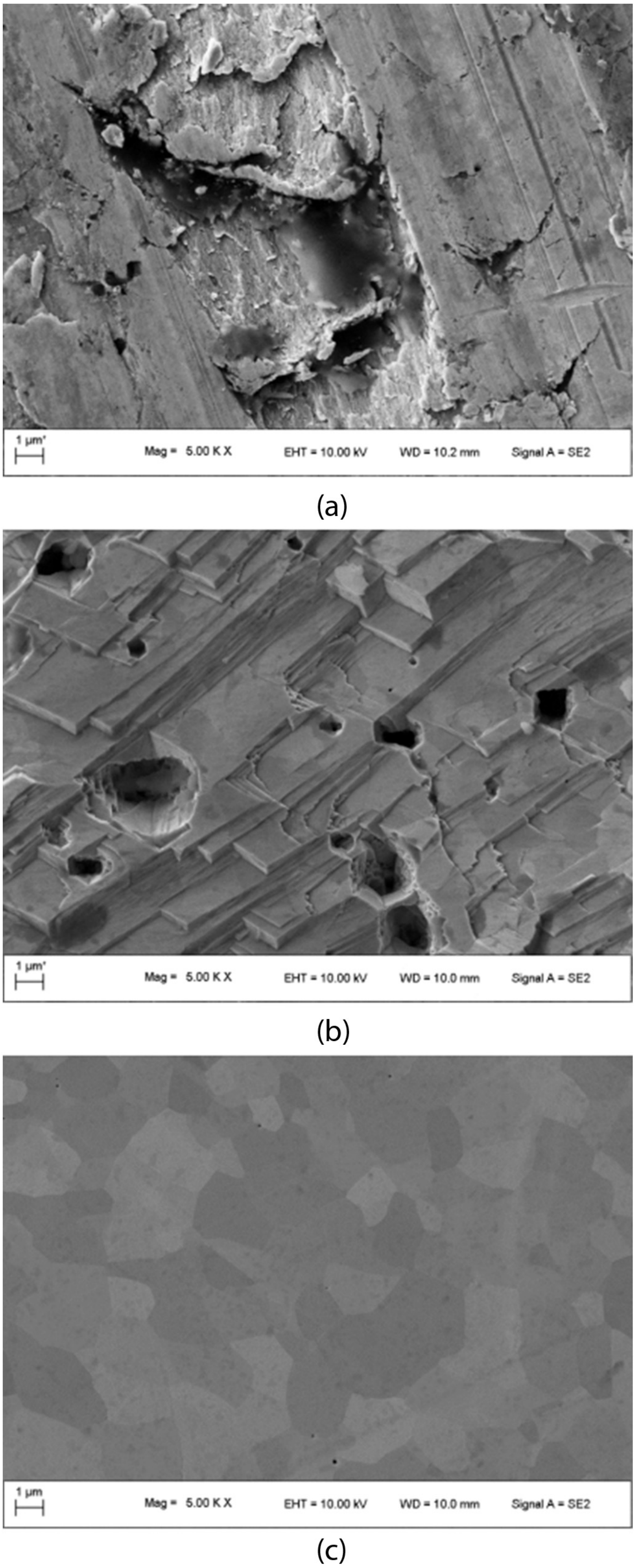


Fig. 4. Voltage and current curves of the proposed two-step ECP process.



(a)

(b)

(c)

Fig. 5. SEM images of tungsten surface. (a) As-ground, (b) after 3 min of current-driven ECP, (c) after 20 min of potential-driven ECP.

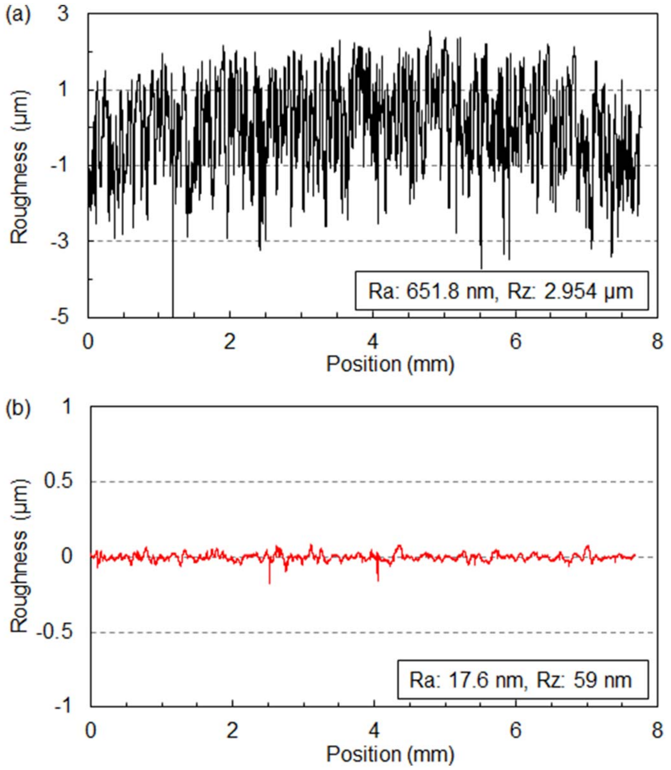


Fig. 6. Surface roughness profiles of the tungsten substrate before (a) and after (b) two-step ECP.

grinding marks and subsurface damage layer could be quickly removed. After the current-driven step, the used electrolyte was replaced by 1 wt % NaOH for conduction of potential-driven ECP. The following potential-driven step lasted for 20 min with a constant voltage of 60 V. According to Fig. 3, the MRR is below 1.0 µm/min, but a smooth surface could be expected.

Fig. 5 shows the change of surface morphology of the tungsten substrate during the proposed two-step ECP process. Before ECP, grinding marks formed by diamond wheels can be observed and the surface was quite rough as shown in Fig. 5(a). After 3 min of current-driven ECP, the grinding marks were removed but the surface hasn't been smoothened as shown in Fig. 5(b) and etching marks including some micro pits were formed. After 20 min of potential-driven ECP, the etching marks formed by the current-driven ECP were completely removed and an ultra-smooth surface was obtained as shown in Fig. 5(c). The final surface is featureless without any sign of intergranular etching. Moreover, the grain boundaries of tungsten can be clearly observed on the polished surface demonstrating that the surface is not only ultra-smooth but also free of damage.

Fig. 6 shows the surface roughness profiles of the tungsten substrates before and after the two-step ECP process. Before electrochemical etching, the Ra roughness of the ground tungsten surface was 651.8 nm. With a total polishing duration of only 23 min, an ultra-smooth surface with an Ra roughness of 17.6 nm has been achieved.

In ECP, anodic oxidation of tungsten and dissolution of the oxide layer are simultaneously occurring. Thus, if anodizing is dominant, there will be a residual oxide layer on the polished surface, which will deteriorate the molding performance of the tungsten substrates. Surface composition before and after the developed two-step ECP process was confirmed using XPS. Fig. 7 shows the W4f spectra measured from the tungsten surface before and after ECP. Compared with the W4f spectra of the as-ground surface as shown in the inset, it was revealed that the oxide layer on the polished surface was even thinner than that on the as-ground surface, which originated from native oxidation. It means that the residual oxide layer in ECP is negligible and it is considered that the mechanical and chemical properties of the substrate will be maintained, which is very important for molding applications.

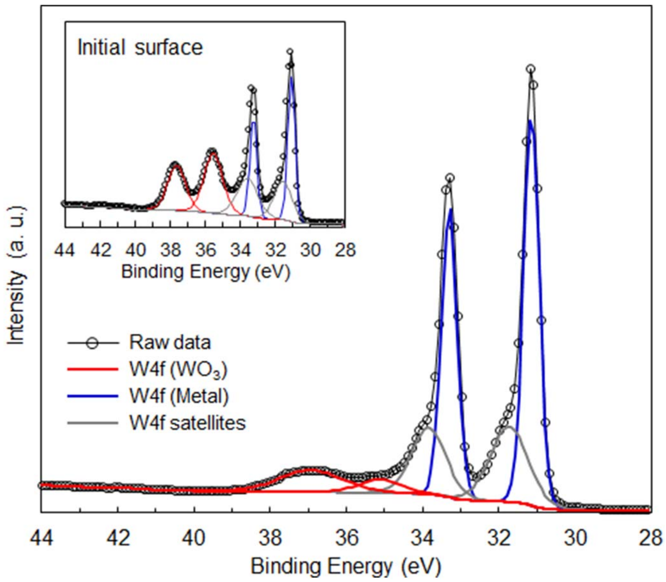


Fig. 7. W4f spectra measured from tungsten surface processed by two-step ECP. The inset figure shows the W4f spectra of the as-ground surface.

4. Conclusions

We demonstrated that the developed two-step ECP process combining the current-driven mode and potential-driven mode is a well-suited polishing approach for tungsten. Current-driven ECP has a very high MRR which enables the quick removal of the grinding marks and subsurface damage. On the other hand, although the MRR of potential-driven ECP is limited, an ultra-smooth surface can be obtained. With a total polishing duration of 23 min, an ultra-smooth and damage-free tungsten surface with an Ra roughness of 17.6 nm has been obtained.

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References

[1] Y. Yamada, M. Kawakubo, K. Kadomura, T. Sugaya, O. Hirai, K. Tsugane, Experimental analysis of pad wear response effect on removal rate variations in tungsten chemical mechanical polishing, J. Electrochem. Soc. 157 (2010) H617–H623.
[2] Y. Mu, R. Han, Y. Sampurno, Y. Zhuang, A. Philipossian, Effect of pad surface micro-texture on removal rate during tungsten chemical mechanical planarization, ECS J. Solid State Sci. Technol. 5 (2016) P345–P348.
[3] B.F. Ju, Y.L. Chen, Y. Ge, The art of electrochemical etching for preparing tungsten probes with controllable tip profile and characteristic parameters, Rev. Sci. Instrum. 82 (2011) 013707.
[4] Y. Khan, H. Al-Falih, Y. Zhang, T.K. Ng, B.S. Ooi, Two-step controllable electrochemical etching of tungsten scanning probe microscopy tips, Rev. Sci. Instrum. 83 (2012) 063708.
[5] N. Suzuki, M. Haritani, J. Yang, R. Hino, E. Shamoto, Elliptical vibration cutting of tungsten alloy molds for optical glass parts, CIRP Ann. Manuf. Technol. 56 (2007) 127–130.
[6] C. Hall, M. Tricard, H. Murakoshi, Y. Yamamoto, K. Kuriyama, H. Yoko, New mold manufacturing techniques, Proc. SPIE 5868 (2005) 58680V.
[7] H. Suzuki, S. Hamada, T. Okino, M. Kondo, Y. Yamagata, T. Higuchi, Ultraprecision finishing of micro-aspheric surface by ultrasonic two-axis vibration assisted polishing, CIRP Ann. Manuf. Technol. 59 (2010) 347–350.
[8] A. Beaucamp, Y. Namba, H. Combrinck, P. Charlton, R. Freeman, Shape adaptive grinding of CVD silicon carbide, CIRP Ann. Manuf. Technol. 63 (2014) 317–320.
[9] A. Beaucamp, Y. Namba, P. Charlton, Process mechanism in shape adaptive grinding (SAG), CIRP Ann. Manuf. Technol. 64 (2015) 305–308.
[10] H. Deng, K. Endo, K. Yamamura, Damage-free finishing of CVD-SiC by a combination of dry plasma etching and plasma-assisted polishing, Int. J. Mach. Tools Manuf. 115 (2017) 38–46.
[11] Y.-J. Seo, N.-H. Kim, W.-S. Lee, Chemical mechanical polishing and electrochemical characteristics of tungsten using mixed oxidizers with hydrogen peroxide and ferric nitrate, Mater. Lett. 60 (2006) 1192–1197.
[12] E. Paul, Application of a CMP model to tungsten CMP, J. Electrochem. Soc. 148 (2001) G359–G363.
[13] N. Ballarin, C. Carraro, R. Maboudian, L. Magagnin, Electropolishing of n-type 3C-polycrystalline silicon carbide, Electrochem. Commun. 40 (2014) 17–19.
[14] D. Zhan, L. Han, J. Zhang, Q. He, Z.W. Tian, Z.Q. Tian, Electrochemical micro/nano-machining: principles and practices, Chem. Soc. Rev. 46 (2017) 1526–1544.
[15] P. Huang, J. Lai, L. Han, F.-Z. Yang, L.-M. Jiang, J.-J. Su, Z.-W. Tian, Z.-Q. Tian, D. Zhan, Electropolishing of titanium alloy under hydrodynamic mode, SCIENCE CHINA Chem. 59 (2016) 1525–1528.
[16] D. Landolt, Fundamental aspects of electropolishing, Electrochim. Acta 32 (1987) 1–11.