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Electrodeposition of metallic tungsten films in $ZnCl_2$–NaCl–KCl–KF–WO_3 melt at 250 °C

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Abstract

WO_3 hardly dissolved in $ZnCl_2$–NaCl–KCl (0.60:0.20:0.20, in mole fraction) melt at 250 °C. The solubility of WO_3 increased by the addition of KF to the melt, which enabled electrodeposition of metallic tungsten. A smooth and fine film of metallic tungsten was obtained on a nickel substrate by the potentiostatic electrolysis at 0.06 V versus Zn(II)/Zn. The thickness reached ca. 2.5 μm after 6-h electrolysis. The surface of the nickel contact probe pin manufactured by the conventional LIGA (Lithographie-Galvanoformung-Abformung, German abbreviation) process was successfully coated with a smooth and adhesive tungsten film by using this melt.

Keywords: Electrodeposition; Molten salt; $ZnCl_2$–NaCl–KCl; Tungsten metal film; Tungsten oxide; Fluoride ion

1. Introduction

Electrodeposition of refractory metals such as tungsten, molybdenum at low temperatures has many advantages from the engineering point of view. One of the most promising applications is the LIGA (Lithographie-Galvanoformung-Abformung, German abbreviation) process, which is a microfabrication technique consisting of lithography, electroforming and molding [1–6]. The importance of applying refractory metals to the LIGA process, which includes coating the conventional LIGA parts with refractory metals, for the Micro-Electro-Mechanical Systems (MEMS) has already been stated in our previous papers [7,8].

For the LIGA process, electrodeposition of metals must be carried out at temperatures lower than 250 ° C due to the limit of heat resistance of the resist sheet. In the case of coating the conventional LIGA parts, electrodeposition temperature should be as low as possible to avoid the softning and embrittlement of the substrate nickel. We have accordingly been studying the electrodeposition of refractory metals in molten salts around 250 °C. We have succeeded in obtaining metallic tungsten [7] and metallic molybdenum [8,9] at 250 ° C using a molten $ZnCl_2$–NaCl–KCl eutectic ($ZnCl_2$:NaCl:KCl = 0.60:0.20:0.20, in mole fraction, m.p. 203 ° C [10]) as an electrolyte. In these previous studies, WCl_4, $MoCl_3$ and $MoCl_5$ were used as tungsten and molybdenum ion sources.

In the present study, electrodeposition of tungsten at 250 ° C was further investigated using WO_3 as a tungsten ion source. As described later, metallic tungsten was not obtained in the melts containing only WO_3. KF was then added to the melt since fine deposits have been obtained in the cases of WCl_4, $MoCl_3$ and $MoCl_5$[7–9]. There is an advantage in using WO_3instead of WCl_4 although tungsten metal can be electrodeposited from WCl_4. It is difficult to use the WCl_4 containing melt for a long time because of the decomposition of WCl_4. On the other hand, WO_3 is much stable in the melt compared with WCl_4. The electrochemical behavior was investigated by cyclic voltammetry. Tungsten films were prepared by potentiostatic electrolysis and the obtained films were analyzed by XPS, SEM and EDX. In

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addition, the electrodeposition of tungsten was applied to coating a contact probe pin manufactured by the conventional LIGA process.

2. Experimental

Experiments were conducted in an argon glove box with a gas circulating purifier (MIWA MFG Co., Ltd.). $ZnCl_2$ (99.9%, Wako Pure Chemical Industries, Ltd.), NaCl and KCl (99.5% each, Wako Pure Chemical Industries, Ltd.) were well mixed into an eutectic composition ($ZnCl_2$:NaCl:KCl = 0.60:0.20:0.20, in mole fraction) and dried in a furnace under vacuum at 130 ° C for 3 days or more. After that, it was melted at 250 ° C in a Pyrex beaker installed in a four-necked separable flask on a heating plate. WO_3 (99.5%, Wako Pure Chemical Industries, Ltd.) and KF (99%, Wako Pure Chemical Industries, Ltd.) were added as tungsten and fluoride ion sources, respectively. A schematic drawing of the experimental apparatus has been shown elsewhere [7]. The working electrode was a nickel plate (99.7%, 5 mm × 10 mm × 0.2 mm, Furuuchi Chemical Corp.) that was fully immersed in the melt. Prior to the experiment, the nickel plate was electrochemically polished in a sulfuric acid, and then immersed in an acid cleaner (Kizai Corp., Kokeisan B) containing $NaHF_2$ to remove surface oxides. A zinc wire (99.99%, 0.5 mm, Nilaco Corp.) immersed in the melt was used as the reference electrode. The counter electrode was a glassy carbon rod (Ø3 mm, GC-20, Tokai Carbon Co., Ltd.). A chromel–alumel thermocouple was used for the temperature measurement. Cyclic voltammetry with positive feedback IR compensation and potentiostatic electrolysis were performed using an electrochemical measurement system (Hokuto Denko Co., Ltd., HZ-5000). The obtained samples were immersed in acetone, and then rinsed with distilled water to remove adherent salts.

The deposits were characterized by scanning electron microscopy (SEM, Hitachi, Ltd., S-2600H), scanning ion microscopy (SIM) with focused ion beam (FIB, FEI Corp., FIB200) cross sectioning, energy dispersive X-ray analysis (EDX, Horiba Co., Ltd., EMAX ENERGY EX-200), X-ray diffraction (XRD, Rigaku Industrial Co., Ltd., Multi Flex) with Cu K α radiation and X-ray photoelectron spectroscopy (XPS, Shimadzu Co., Ltd., ESCA-3200).

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry was performed using a nickel electrode after the addition of WO_3 (0.54 mol% added) in $ZnCl_2$–NaCl–KCl melt at 250 °C. The shape of the voltammogram did not change by the addition of WO_3. It was observed that WO_3 hardly dissolved in $ZnCl_2$–NaCl–KCl melt. Accordingly, no tungsten deposit was obtained by electrolysis in the $ZnCl_2$–NaCl–KCl–WO_3 melt.

Since fluoride melts generally have higher solubilities of metal oxides than chloride melts, KF was added as a fluoride ion source to increase the solubility of WO_3. Moreover, fine deposits have been obtained by the addition of KF in our previous studies, in which WCl_4, $MoCl_3$ and $MoCl_5$ were used as refractory metal ion sources [7–9]. Before investigating the (KF + WO_3) added melt, cyclic voltammetry was carried out for the only KF added melt. A gray curve in Fig. 1 shows a cyclic voltammogram obtained at the nickel plate electrode in $ZnCl_2$–NaCl–KCl–KF (4 mol% added) melt. The shape of the cyclic voltammogram was identical to that obtained in the original $ZnCl_2$–NaCl–KCl melt. Cathodic and anodic current peaks around 0 V versus Zn(II)/Zn are attributed to the deposition and dissolution of metallic zinc, respectively. Meanwhile, a cathodic current peak around 0.03 V and an anodic current peak around 0.12 V are attributed to the formation and dissolution of Ni–Zn alloy [7], respectively.

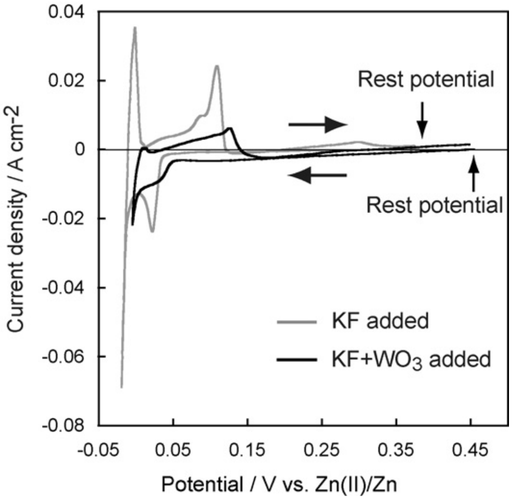

Fig. 1. Cyclic voltammograms at nickel electrodes in $ZnCl_2$–NaCl–KCl–KF (4 mol% added) melt (gray curve) and $ZnCl_2$–NaCl–KCl–KF (4 mol% added)–WO_3(0.54 mol% added) melt (black curve) at 250 °C. Scan rate : 0.05 V s^{-1}.

In the (KF + WO_3) added melt, it was observed that WO_3 dissolved in the melt and the color of the melt changed from colorless to gray. The dissolution of WO_3 probably proceeded by the formation of oxo-fluoro tungsten complex ions. A certain portion of WO_3, however, remained undissolved. Thus, the melt is regarded as saturated with WO_3. A black plot in Fig. 1 shows a cyclic voltammogram measured for the nickel plate electrode in the $ZnCl_2$–NaCl–KCl–KF (4 mol% added)–WO_3 (0.54 mol% added) melt at 250 °C. A new cathodic current is observed in the potential region of 0.05–0.45 V, suggesting electrodeposition of metallic tungsten. Neverthless, the current peak which is often observed for the electrodeposition of metals in high temperature molten salts [11,12] did not appear in the present case. The shape change of the voltammogram in the potential region of 0–0.03 V is explained by the deposition of tungsten, suppressing both the deposition of pure zinc and the formation of Ni–Zn alloy.

3.2. Potentiostatic electrolysis and characterization of deposit

Since electrodeposition of tungsten was speculated to occur in the potential region lower than 0.45 V, potentiostatic elec-

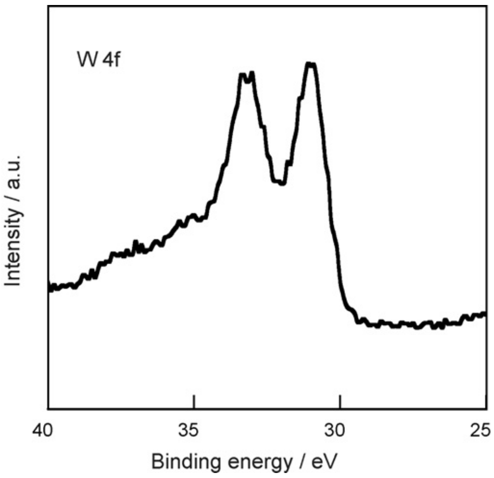

Fig. 2. A W 4f XPS spectrum of the film obtained by potentiostatic electrolysis at 0.06 V vs. Zn(II)/Zn for 3 h in $ZnCl_2$–NaCl–KCl–KF (4 mol% added)–WO_3 (0.54 mol% added) melt at 250 °C. Argon ion etching time: 4500 s.

trolysis was performed at 0.06 V for 3 h, where deposition of tungsten was expected and that of zinc was not. After the potentiostatic electrolysis, a bright brown film was obtained. Fig. 2 shows an XPS spectrum of W 4f for the deposit after argon ion etching for 4500 s. W $4f_{5/2}$ and W $4f_{7/2}$ peaks corresponding to metallic tungsten are observed at 33 and 31 eV, respectively [13]. Since the peaks ascribed to other oxidation state of tungsten are not observed, deposition of composite coatings of W and undissolved WO_3 is negligible. On the other hand, the XRD pattern did not show any distinctive peak corresponding to the metallic tungsten crystal [14], indicating that the obtained tungsten was amorphous. EDX results showed that the chlorine content was less than 1 at%, proving that melt inclusion did not occur during the electrodeposition.

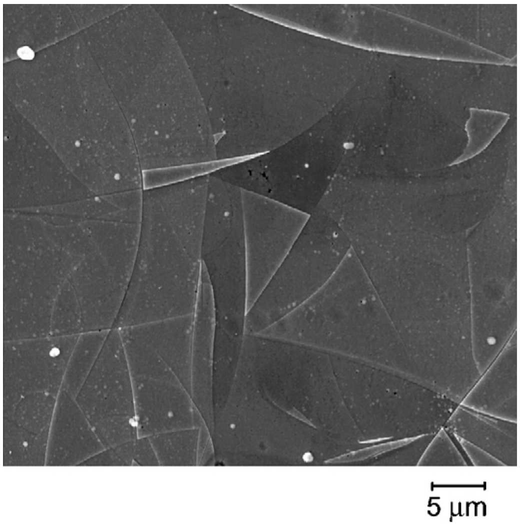

Fig. 3. A surface SEM image of the film obtained by potentiostatic electrolysis at 0.06 V vs. Zn(II)/Zn for 3 h in $ZnCl_2$–NaCl–KCl–KF (4 mol% added)–WO_3 (0.54 mol% added) melt at 250 °C.

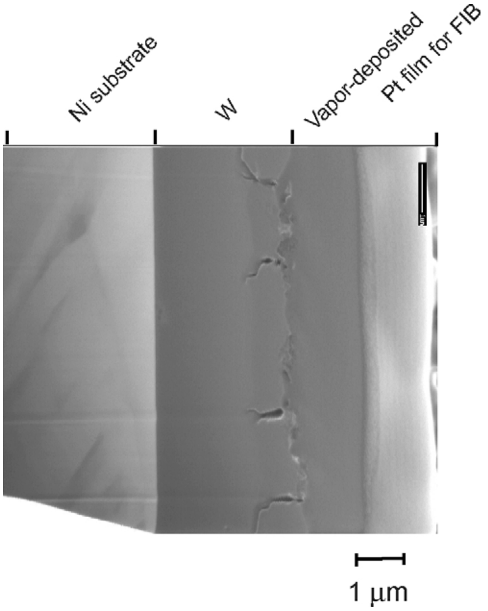

Fig. 4. A cross-sectional SIM image of the film obtained by potentiostatic electrolysis at 0.06 V vs. Zn(II)/Zn for 6 h in $ZnCl_2$–NaCl–KCl–KF (4 mol% added)–WO_3 (0.54 mol% added) melt at 250 °C.

Fig. 3 shows a surface SEM image of the film. Although there are some microcracks, the surface is quite smooth on the whole. The microcracks indicate that tensile stress was generated on the deposited film. There are two possibilities for the tensile stress. One is the coefficient of thermal expansion (CTE) mismatching and the other is the deposition-induced internal stress. Here, the CTE mismatching is excluded since CTE of nickel is larger than that of tungsten, which gives rise to compressive stress. Thus, the microcracks would be produced by the deposition-induced tensile stress. Fig. 4 shows a cross-sectional SIM image of a film obtained by potentiostatic electrolysis at 0.06 V for 6 h. To obtain the cross-sectional image, the FIB cross sectioning was conducted after platinum was vapor-deposited on the surface of the deposit. The milling was firstly performed with gallium ion beam at acceleration voltage of 30 kV and current of 1000 pA for 2 h. Subsequently, the milling at acceleration voltage of 30 kV and current of 350 pA was carried out for 30 min. The film is dense and the thickness is ca. 2.5 μm. The microcracks of ca. 0.8 μm long are also observed in the surface region, which is possibly due to the deposition-induced internal stress as explained above.

Finally, to confirm the feasibility of the present method as a new tungsten coating technique, electrodeposition was conducted for a nickel contact probe pin. The contact probe pin is manufactured by the conventional LIGA process and is practically used for semiconductor testing. In the present experiment, the probe pin was coated with rhodium prior to the electrodeposition to prevent the Ni–Zn alloy formation. The electrodeposition was carried out at 0.06 V for 2 h in the $ZnCl_2$–NaCl–KCl–KF (4 mol% added)–WO_3 (0.54 mol% added) melt at 250 °C. As shown in Fig. 5, a smooth and adhesive film desired was obtained on the probe pin. Since tungsten is potentially superior to nickel in thermal stability and mechanical strength, the performance and durability of the probe pin is expected to be improved largely by this method. Moreover, the present method is promising as a new method of tungsten coating which can be applied to various

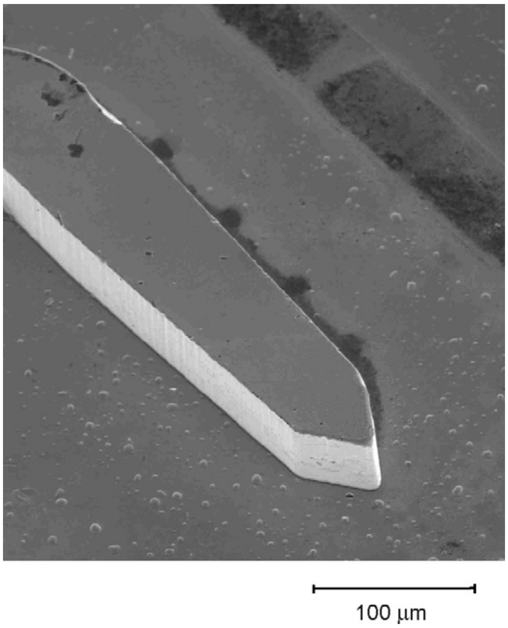

Fig. 5. An SEM image of the nickel-made contact probe pin coated with tungsten film by potentiostatic electrolysis at 0.06 V vs. Zn(II)/Zn for 2 h in $ZnCl_2$–NaCl–KCl–KF (4 mol% added)–WO_3 (0.54 mol% added) melt at 250 °C.

kinds of materials including LIGA microparts due to the low process temperatures.

4. Conclusion

WO_3 hardly dissolved in $ZnCl_2$–NaCl–KCl (0.60:0.20:0.20, in mole fraction) melt at 250 °C. After the addition of KF to the melt, however, WO_3 dissolves in the melt and a smooth and dense tungsten film is obtained at 250 °C. The surface of a nickel contact probe pin manufactured by the conventional LIGA process was successfully coated with tungsten by using this melt. The present method is promising as a new tungsten coating method at low temperature.

Acknowledgments

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