ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 9, No. 4. 2003

Electrolyte Considerations of Electrodeposited Ni-W Alloys for Microdevice Fabrication

H. Cesiulis[1]*, E. J. Podlaha-Murphy[2]

[1]*Department of Physical Chemistry, Faculty of Chemistry, Vilnius University, Naugarduko 24, LT-2006 Vilnius, Lithuania*
[2]*Gordon A. and Mary Cain Department of Chemical Engineering, Louisiana State University,*
Baton Rouge, LA 70803, USA

Received 08 September 2003; accepted 13 October 2003

Electrodeposited systems that contain gas evolving side reactions, such as NiW, can be problematic for deep micro-recessed electrodes. A limiting factor for the adaptability of conventional plating baths to deep recess plating is the variance in hydrodynamic conditions. For Ni-W electrodeposition in citrate-ammonium electrolytes, buffering capacity and pulse plating has been considered to circumvent local pH rises accompanied by the side reaction. Based on simulated solubility data and determined buffer capacity the following composition for Ni-W electroplating was proposed: $NiSO_4$ – 0.2 M; Na_3Citr – 0.5 M; Na_2WO_4 – 0.4 M; Na_2CO_3 – 0.5 M; NH_3 water – 1.2 M; $t = 70\,°C$; pH 8.5 – 9; j = 10 – 60 mA cm^{-2} for alloys containing 9 – 15 wt.% of W. In the presence of CO_3^{2-} the alloy composition is less dependent upon j and pH than in the absence of it. For better distribution of metal on the patterns, the pulse current deposition should be applied.

Keywords: recesses, nickel alloys, tungsten alloys, electrodeposition, microfabrication.

1. INTRODUCTION

Micro Electronic Mechanical Systems (MEMS) is a burgeoning new technology, which exploits the existing microelectronics infrastructure to create complex machines with micron feature sizes. These machines can have many functions, including sensing, communication and actuation. The miniature components for these machines often require electrodeposition fabrication steps into deep recesses produced by lithographic techniques, such as X-ray lithography or photolithography. The LIGA technique (German acronym: Lithograhie, Galvanoforming, Abformung) is being widely used to generate microstructures with high aspect ratios [1]. The process consists of a lithographic step during which an absorber pattern is transferred to a resist layer by shadow printing with synchrotron radiation. This is followed by electroplating into the recessed pattern. The electroplated microstructures can then be used as final products or as mold inserts to replicate structures through processes like injection molding, reaction injection molding, hot-embossing, slip casting or extrusion [1 – 3].

Electrodeposited nickel is one of the most widely employed materials in the fabrication of micro machines, such as micro-gears, micro-cantilevers, etc., and their components. However, the use of Ni is limited when properties like mechanical strength, thermal stability, hardness, wear and corrosion resistance, are desired. Alloys with tungsten provide the obvious alternatives. Ni-W alloys have been employed for the manufacture of microstructured tools (e.g. heat microexchangers) with excellent mechanical properties regarding wear and mechanical durability [1, 4], premium hardness [5 – 6], reasonable structure and surface properties [7]. Significant research has gone into plating different alloys from a wide variety of electrolytes onto flat surfaces. For Ni-W electrodeposition two main types of alkaline solutions were developed: based on the pyrophosphate Ni(II) complexes [8], and another based on the Ni(II) citrate complexes e.g. [9 – 12], and better developed. However, the plating conditions (i.e. current density) in those findings do not always translate to produce the same outcome in recesses of different geometries and sizes. The major limiting factor for the adaptability of conventional plating baths to deep recess plating is the variance in hydrodynamic conditions. Namely, despite electrolyte agitation at the mouth of the recess, the electrolyte in the recess remains stagnant creating transport limitations of the reactant species and an undesirable accumulation of unwanted product species. In addition, reactions inherent to the iron-group and W-alloy electrodeposition often occur with gas evolving side reactions and hydroxyl ion products that can lead to large pH rises.

Therefore, the aim of this work is to clarify factors allowing deposition of Ni-W alloys in deep recesses under reasonable rates and alloys composition. For this purpose citrate-ammonium electrolytes were adapted, because of the wide range of W deposit composition obtained, high deposit microhardness, fine texture, and smooth surface morphology [6].

2. EXPERIMENTAL PROCEDURE

Ni-W films were deposited on a rotating cylinder electrode using copper as a substrate at 100 rpm. Before electrodeposition they were polished, rinsed in 10 % sulfuric acid for removal of any oxides using a 1510 Bransonic® ultrasonic bath cleaner and then degreased using acetone. A Pine instrument company Analytical Rotator Model AFMSRX was used to operate RCE at different rotation rates. A platinum plated titanium mesh

---

*Corresponding author. Tel.: + 370-5-2336419; fax:+ 370-5-2330987.
E-mail address: *henrikas.cesiulis@chf.vu.lt* (H. Cesiulis)

was used as the counter electrode. Cathodic and anodic compartments were separated by glass frits.

The substrate for deep recess electrodeposition consists of four different layers, which are Cu, CuO, layer of bonding solution, and polymethylmethacrylate (PMMA). The photoresist was patterned by exposure to X-ray radiation through a mask having the desired pattern at the LSU Center for Advanced Micro Devices (CAMD). The exposed regions were dissolved away by developing using a *developer* solution, *pre-rinse* and *rinse* solutions. The constituents of solutions are provided in Table 1. The developing process consisted of four cycles of sonication, each consisting of developing in *developer* solution for 10 min, rinsing in *pre-rinse* solution, which is an old rinse solution for 2 min, and rinsing in *rinse* solution for 1 hr. The substrate was then etched in *CuO-etching* solution for 2 min or until the copper oxide is completely removed.

Table 1. Recipes (in mL) of solutions used for patterns preparation

Developer solution	Diethylene glycol butyl ether – 600; morpholine – 200; 2-minoethanol – 50; water – 150
Pre – rinse solution	Old rinse solution
Rinse solution	Diethylene glycol butyl ether – 800; water - 200
Copper oxide etch solution	KCl – 0.5 M; HCl – 0.5 M

The Deep Recess Electrode (DRE) was placed into a jig to hold it in place during electrodeposition. The jig has two cylindrical disks, which are held together using nylon screws. The bottom disk has a copper plate recessed to seat the copper substrate. A copper wire soldered to the bottom of the recessed plate served as the cathode connection. The top disk has an opening that enables the electrolyte solution to reach the substrate. A Ni sheet placed approximately 2 – 3 cm above the jig served as the anode. A stir bar was used to provide bulk mixing. The cell assembly was then lowered into a hot water bath maintained at 70 °C using a Fisher Scientific isotemp® Model 2100 water pump heater.

Ni-W alloys were obtained under galvanostatic conditions controlled by EG&G Princeton Applied Research Potentiostat/Galvanostat, Model 363.

Composition analysis of the deposits on the copper cylinders was done by using Kevex Omicron X-ray Fluorescence Spectroscope. The morphology of the deposits was obtained by a Scanning Electron Microscope (SEM) (Joel JSM-840A).

The electrodeposition of Ni-W alloys was performed in the solution containing: $NiSO_4 + Na_2WO_4 + Na_3Citr +$ $+ NH_3$ water. Some solutions contained 0.5 M Na_2CO_3. The bath pH for Ni-W electrodeposition was adjusted by adding NH_3 water. As follows from the study carried out, (see Fig. 1), the pH is a function of the amount of NH_3 added to the electrolyte when the desired pH is below 9.0 – 9.5. However, at 70 °C when pH ~10, an excess of ammonia is sufficient to maintain that pH. From 1 – 2 M NH_3 the pH is insensitive to the NH_3 concentration at the high electrolyte temperature. At pH ~10 at 25 °C the electrolyte pH is again sensitive to ammonia addition. Therefore, to improve reproducibility of the obtained results, the study was carrying out under the constant concentration of NH_3 that was enough to maintain the pH at a value of 10 (1.2 M). If lower electrolyte pH was desired in the range pH < 10 then the electrolyte was adjusted by adding of conc. H_2SO_4.

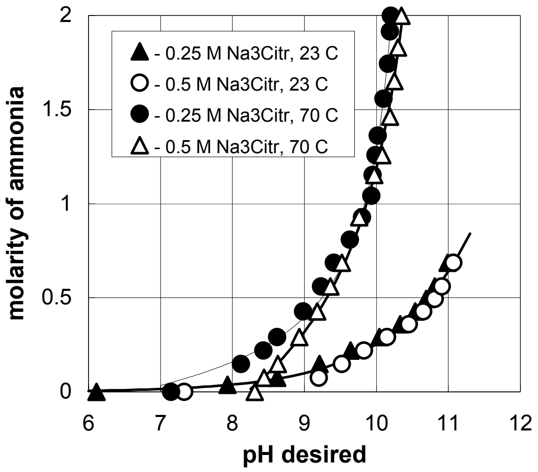

Fig. 1. Molarity of ammonia water required for the desired pH of the baths electrolytes at various concentrations of Ni_3Citr and temperatures

3. RESULTS AND DISCUSSIONS

Methodology for bath solution design. The main challenge of electrodeposition in deep recesses is that the larger inherent mass transport boundary layers creates a largely diffusion controlled reaction. In the case of Ni-W electrodeposition the electroreduction of WO_4^{2-}-ion to W is associated with increasing of pH in the reaction layer:

$$WO_4^{2-} + 4H_2O + 6e = W + 8OH^-.$$

Additionally, the overvoltage for hydrogen evolution:

$$2H_2O + 2e = H_2 + 2OH^-$$

is lower on the Ni-W than that on the pure Ni and also yields an increase in the local pH at the bottom of the recesses. Solubility limits have therefore been examined. Based on equilibrium constants [13] corrected for higher ionic strength in accordance with Debye-Hückel theory for elevated ionic strengths, the solubility of $NiSO_4$ in the citrate-ammonia baths was simulated. The total number of chemical equilibrium reactions included was 26 with 26 unknowns solved by method used in Maple 6 software. The results are shown in Fig. 2.

Shown in Fig. 2, the solubility of $NiSO_4$ depends upon citrate concentration, and decreases with an increase of pH. The solubility decreases particularly at pH > 10, where precipitation of $Ni(OH)_2$ is predicted. Considering the small volume of solution in micro-recesses the forming OH^- could cause a sufficient increase in local pH, resulting in precipitation and sequentially terminating electrolysis. Thus, based on the data presented in Fig. 2, the precipitation of $Ni(OH)_2$ is predicted at pH > 10. However, at room temperature, simulated at 23 °C the solution

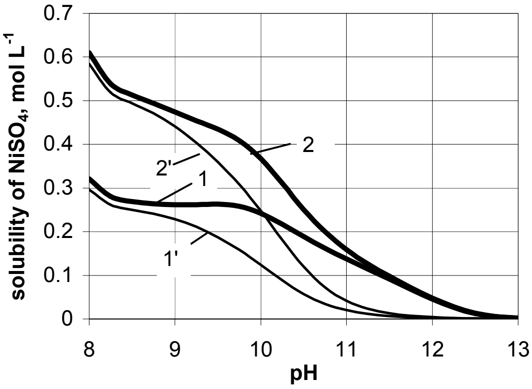

Fig. 2. Simulated solubility of $NiSO_4$ at 23 °C as a function of pH of citrate-ammonia baths in the absence of NH_3 water (fine lines 1' and 2') and in the presence of 1.2 M of NH_3 water (solid lines 1 and 2) in citrates:
1, 1' – 0.25 M Na_3Citr; 2, 2' – 0.50 M Na_3Citr

remains stable due to slow exchange reactions between nickel complexes and OH^- - ions [6], for example:

$$Ni(HCitr)^- + 2OH^- \rightarrow Ni(OH)_2 + HCitr^{3-};$$
$$Ni(HCitr)_2^{4-} + 2OH^- \rightarrow Ni(OH)_2 + 2HCitr^{3-}$$
$$NiCitr^{2-} + OH^- \rightarrow Ni(OH)_2 + Citr^{4-}$$
$$Ni(NH_3)_{1-6}^{2+} + 2OH^- \rightarrow Ni(OH)_2 + (1-6)NH_3(aq)$$

The precipitation points are summarized in Table 2.

Table 2. pH at which the precipitation of $Ni(OH)_2$ is obtained at 70 °C. The common components of solutions are: 0.2 M $NiSO_4$ + 0.4 M Na_2WO_4 + 1.2 M NH_3 water

Additional components and concentrations	pH of $Ni(OH)_2$ precipitation at 70 °C
0.25 M Na_3Citr	10.47
0.5 M Na_3Citr	10.55
0.25 M Na_3Citr + 0.5 M Na_2CO_3	10.86
0.5 M Na_3Citr + 0.5 M Na_2CO_3	10.60

The electrolyte composition considered here has been chosen to ensure stability even if the pH rises up to 1.6 units from the evolution of OH^- on the cathode. In addition, an increase in pH causes the tungsten amount in the alloys to decrease. Moreover, the electrodeposition from aqueous baths generally is carried out in non-hermetic cells. In this case, the sufficient part of ammonia could evaporate during long-term electrodeposition at elevated temperatures that result in a decreasing pH as well as in deposition rate. In order to avoid the decrease in pH when a part of ammonia evaporates, Na_2CO_3 was introduced into the electrolyte maintain the desired pH.

Electrodeposition of Ni-W alloys is accompanied by H_2 evolution yielding an alkalization of a pre-electrodic layer, that might result in precipitation of $Ni(OH)_2$ [6], that decreases the deposition rate or stops it, and can decrease the W content [8, 14]. To obtain stable characteristics of deposits in recesses of large thickness (e.g. >100 μm) the solutions must possess sufficient buffer capacity. The buffer capacity of various solutions is shown in Fig. 3. As shown, in the presence of 1.2 M aqueous NH_3 the dependence trends are similar for the two electrolyte temperatures considered. Maximal values of buffer capacity are obtained at pH 9.3 – 9.7 (25 °C) and at pH 8.5 – 8.8 (70 °C), and minimal values in the alkaline range of pH at pH 11 9.3 – 9.7 (25 °C) or at pH ~10 (70 °C).

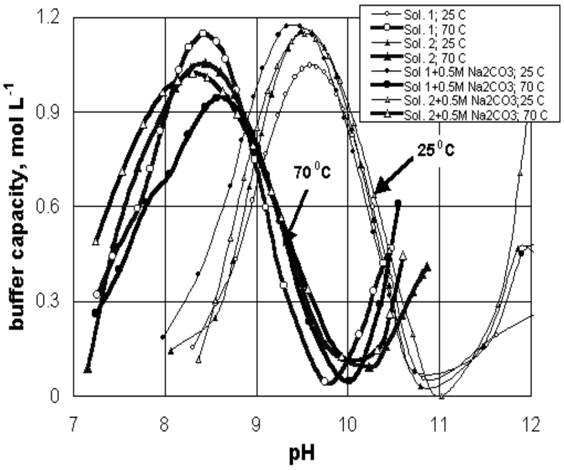

Fig. 3. Experimentally obtained buffer capacity of solutions as a function of pH at various temperatures. Main components:
Sol. 1: 0.2 M $NiSO_4$ + 1.2 M NH_3 + 0.25 M citric acid + + 0.4 M Na_2WO_4;
Sol. 2: 0.2 M $NiSO_4$ + 1.2 M NH_3 + 0.50 M citric acid + + 0.4M Na_2WO_4

Ni-W electrodeposition on RCE. For further examination we selected a solution containing 0.5 M Na_3Citr ensuring solution stability. The electrodeposits of Ni-W alloys were obtained on the RCE (100 rpm) in the solution containing: 0.2 M $NiSO_4$ + 0.4 M Na_2WO_4 + + 0.5 M Na_3Citr + 1.2 M NH_3 (*Sol. 3*) at various pHs adjusted by H_2SO_4. Some of the solutions contained 0.5 M Na_2CO_3, to evaluate any changes in deposit composition, and as an alternative buffer to NH_3, as it evaporates during long term electrolysis. The influence of current density on the W amount in Ni-W alloys is shown in Fig. 4.

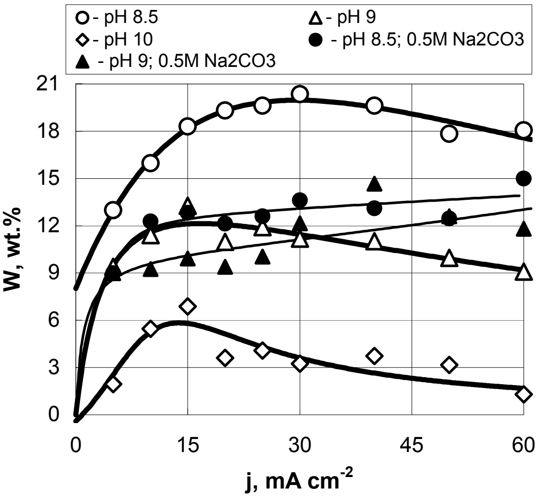

Fig. 4. Content of W in Ni-W alloys as a function of current density at various pH. Alloys were obtained from solutions (*Sol. 3*) with or without Na_2CO_3 (at concentration 0.5 M)

If Na_2CO_3 is absent in the solutions the W amount in the alloys is more sensitive to pH than the current density. There is a large difference in deposit composition comparing pH 8.5 and 10 without Na_2CO_3. Surprisingly, the adding of Na_2CO_3 into the bath reduces the influence of pH as well as of current density on W amount in the alloys. During electrodeposition in recesses or on the other devices with complicated shape, distribution of electric fields and potentials became also complicated that cause non-uniformity of local current densities in some spots. The weak dependence of W amount on current density is desirable for this kind application in order to obtain deposits having uniform composition on the entire device.

The current efficiency is inversely proportional to the current density applied whereas the effect of bath composition is rather weak (see Fig. 5). Such dependence is governed by side reaction concurrent with Ni and W deposition, and is associated mostly with hydrogen evolution that depends on the current density and does not depends on the bath composition.

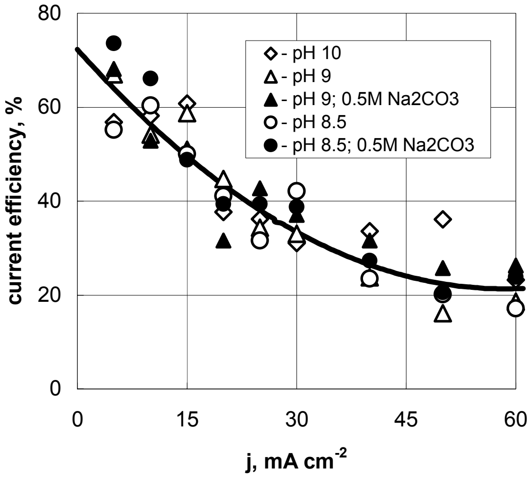

Fig. 5. Current efficiency for Ni-W alloys electrodeposition as a function of current density at various pH. Alloys were obtained from solutions (*Sol. 3*) with or without Na_2CO_3 (at concentration 0.5 M)

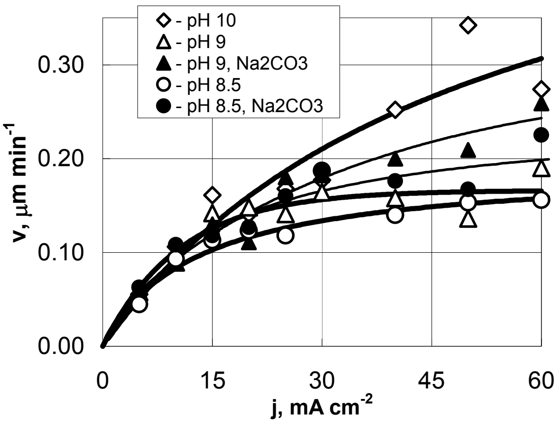

Fig. 6. Deposition rates of Ni-W alloys as a function of current density at various pH. Alloys were obtained from solutions (*Sol. 3*) with or without Na_2CO_3 (at concentration 0.5 M)

Fig. 6 presents the deposition rate. The values of this parameter are governed by both the current efficiency and the alloy composition. Such dependences were determined by the partial current densities for Ni and W co-deposition under the assumption that densities of separate metals and their in alloys are the same. In the case of Ni-W electrodeposition from investigated solutions, the deposition rates depend sufficiently on the bath composition as well as on the current density applied when current densities are higher than 15 – 20 mA cm^{-2}.

Solution behavior during long-term electrolysis. Solutions dedicated for alloys electrodeposition in deep recesses should provide stable characteristics and uniform alloy composition during the course of the entire long-term deposition.

For the electrodeposition of Ni-W alloys in micro-recessed patterns (depth of recesses – 500 µm, diameter of holes – 180 µm, number of holes in pattern – 11040) the bath conditions were pH 9, and DC current density as 15 mA cm^{-2}. Under such conditions the solution possesses reasonable buffer capacity, deposition rate, and alloys contain reasonable amount of tungsten. The comparative results for baths with and without carbonates are presented in Table 3. In the bath without carbonates they do not obtained stable deposition characteristics after 14 hours electrodeposition. In this bath, the evaporation of some part amount of NH_3 results in a decrease in pH and deposition rate due to increasing amount of W in alloy. In the bath containing carbonates the stable deposition characteristics are obtained even after 45 hours electrodeposition and are closed to initial values.

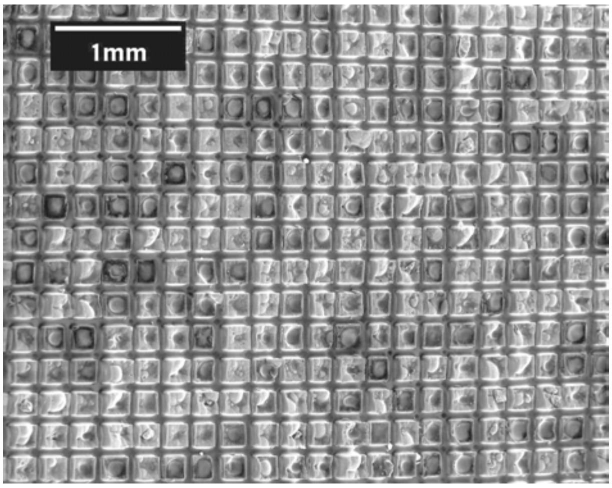

Fig. 7. SEM micrograph of Ni-W (6.7 wt.% W) microposts obtained by pulsing current (j = 15 mA cm^{-2}, ON – 10 s, OFF – 30 s) from the solution: $NiSO_4$ – 0.2 M; Na_3Citr – 0.5 M; Na_2WO_4 – 0.4 M; Na_2CO_3 – 0.5 M; NH_3 water – 1.2 M; pH 9, 70 °C

However, the throwing power of solution is not sufficient to obtain an even distribution of alloy in the recesses under DC mode, and should be improved. A better distribution was obtained under pulse current electrodeposition (see Fig. 7), boundaries are well formed and coating is dense.

4. CONCLUSIONS

Ammonia-citrate electrolytes with and without carbonates were investigated for micro-fabrication of NiW parts. Buffer capacity was found to be a function of the electrolyte temperature. Electrolytes containing carbonates

Table 3. The results of Ni-W alloy electrodeposition on the patterns from citrate-ammonia solutions without and with carbonates. pH 9 (adjusted by H_2SO_4); temperature 70 °C; current density 15 mA cm^{-2} The data were obtained on RDE (at 100 rpm) before and after electrolysis on the patterns

Parameters	Bath composition (1): $NiSO_4$ – 0.2 M; Na_3Citr – 0.5 M; Na_2WO_4 – 0.4 M; NH_3 water – 1.2 M		Bath composition (2): $NiSO_4$ – 0.2 M; Na_3Citr – 0.5 M; Na_2WO_4 – 0.4 M; Na_2CO_3 – 0.5 M; NH_3 water – 1.2 M	
	At the beginning of deposition	At the end of deposition	At the beginning of deposition	At the end of deposition
Deposition time, hours	14		45	
pH	9.0	7.39	9.0	8.6
Content of W, wt.%	13.38	19.29	9.39	11.43
Deposition rate, μm min^{-1}	0.142	0.0873	0.114	0.120
Current efficiency, %	58.74	60.40	44.9	47.8
Partial current densities, mA cm^{-2}:				
for Ni	5.25	4.41	4.61	4.53
for W	3.56	4.66	2.12	2.61
side reaction	6.19	5.93	8.27	7.83

were more robust as the deposit composition was less sensitive to the electrolyte pH and applied current density. Thus, ammonia-citrate NiW electrolytes with the addition of Na_2CO_3 is suggested as a more reliable electrolyte choice in micro-recess patterned electrodes when deposit uniformity is desired.

Acknowledgments

Authors acknowledge the US National Science Foundation and Lithuanian Science and Study Foundation (grant C 03047) for partial financial support.

REFERENCES

1. **Romankiw, L. T.** A Path: From Electroplating through Lithographic Masks in Electronics to LIGA in MEMS *Electrochemica Acta* 42 (20 – 22) 1997: pp. 2985 – 3005.
2. **Lowe, H., Ehrfeld, W., Diebel, J.** Ultraprecision Micro-electroforming of Metals and Alloys *Proceeding of SPIE* 3223 1997: pp. 168 – 175.
3. **Ehrfeld, W., Hessel, V., Lowe, H., Schulz, Ch., Weber, L.** Materials of LIGA Technology *Microsystem Technologies* 5 1999: pp. 105 – 112.
4. **Hubbart Jr., P. B., Podlaha, E. J.** The Study of Induced Codeposition of Ni-W alloys *1997th Meet. – Toronto, Canada,* May 14 – 18, 2001.
5. **Donten, M.** Bulk and Surface Composition, Amorphous Structure, and Thermocrystallization of Electrodeposited Alloys of Tungsten with Iron, Nickel and Cobalt *J. Solid State Electrochem.* 3 1999: pp. 87 – 96.
6. **Cesiulis, H., Baltutiene, A., Donten, M., Donten, M. L., Stojek, Z.** Increase in Rate of Electrodeposition and in Ni(II) Concentration in the Bath as a Way to Control Grain Size of Amorphous / Nanocrystalline Ni-W Alloys *J. Solid State Electrochem.* 6 2002: pp. 237 – 244.
7. **Donten, M., Stojek, Z., Cesiulis, H.** Formation of Nanofibres in Thin Layers of Amorphous W Alloys with Ni, Co and Fe Obtained by Electrodeposition *J. Electrochem. Soc.* 150 (2) 2003: pp. C95 – C98.
8. **Cesiulis, H., Donten, M., Donten, M. L., Stojek, Z.** Electrodeposition of Ni-W, Ni-Mo and Ni-Mo-W Alloys from Pyrophosphate Baths *Materials Science* (*Medžiagotyra*) 7 (4) 2001: pp. 237 – 241.
9. **Franz, S., Marlot, A., Landolt, D.** Pulse Plating of Ni-W Alloys *204th ISE Meeting*, 2004, abst. 697.
10. **Donten, M., Cesiulis, H., Stojek, Z.** Electrodeposition and Properties of Ni-W, Fe-W and Fe-Ni-W Amorphous Alloys. A Comparative Study *Electrochim. Acta* 45 (11) 2000: pp. 3389 – 3396.
11. **Chlein-Ho Huang.** A Study of the Effects of Diammonium Citrate on the Electroformed Nickel-tungsten Alloy *Plating & Surf. Finishing* 84 (4) 1997: pp. 62 – 65.
12. **Yamasaki, T., Tomohira, R., Ogino, Y., Schlossmacher, P., Ehrlich, K.** Formation of Ductile Amorphous & Nanocrystalline Ni-W Alloys by Electrodeposition *Plating & Surf. Finishing* 87 (5) 2000: pp. 148 – 152.
13. **Kotrý, S., Šůcha, L.** Handbook of Chemical Equilibria in Analytical Chemistry. - New York: Ellis Horwood Ltd., 1985.
14. **Donten, M., Cesiulis, H., Stojek, Z.** Electrodeposition and Properties of Ni-W, Fe-W and Ni-Fe-W Amorphous Alloys. A Comparative Study *Electrochimica Acta* 45 (20) 2000: pp. 3389 – 3396.