Electrochemical Deposition of Nickel for Micro-mechanical Systems

PAULA PRIOTEASA[1]*, AURORA PETICA[1], MARIUS POPA[1], CRISTINEL ILIE[1], TEODOR VISAN[2]

[1] INCDIE ICPE, Advanced Research, 313 Splaiul Unirii, 030138, Bucharest, Romania

[2] University Politehnica Bucharest, Department of Applied Physical Chemistry and Electrochemistry, 3-7 Polizu Str., 011061, Bucharest, Romania

Parts of micro-mechanical systems were obtained electrochemically from nickel sulfamate-based electrolyte on silicon wafer substrate using LIGA lithography. A selection of optimum fabrication sequences and operating conditions was also done. The deposited nickel layer showed good appearance especially for relatively thin nickel layers (up to 80-90μm), characterized by uniformity, fine-grained and brightness. In the cases of thicker layer (more than 90-100μm) dull and rough deposit, as well as dendrites are noticed on the edge zone of the substrate mold. The structure, texture, crystallite size and Vickers microhardness were evidenced and measured by optical and SEM microscopy, XRD diffraction spectroscopy and microhardness tests.

Keywords: micro-mechanical systems, nickel electrodeposition, sulfamate bath,surface characterization

In modern surface treatment technologies nickel is the most frequently used, over 15% of products being covered with nickel deposit. The nickel layers have an extensive array of application areas, from protective decorative coatings required in electrical engineering, electronics or machine building, for processing microelectronic components, micro-electro-mechanical systems (MEMS) or high-precision microstructures, including biological microstructures.[1] Thanks to scientific progress of recent years, theoretical aspects of electrochemical engineering underlying electrochemical processes of micro-manufacturing have been developed considerably. Thus, in association with advanced techniques and equipment, they lead to the development of metallic materials with controlled micro- and nanostructures, that can be deposited as layers on miniaturized components.

Manufacture of microparts requires increased control of all their properties and a deep understanding of the *operating parameters-microstructure-properties* correlation. In the specialty literature numerous comparative experimental results on the selection of process parameters have been published, in order to achieve optimal microstructure of Ni deposits [2,3]. However, the works that analyze the influence of process parameters on the microstructure and properties of nickel deposits are much fewer [4-12].

In recent years, nanostructured materials have found increasing interest due to their special properties in different areas [13-16]; some examples are: nanoelectronics, photonics, thermoelectronics, to creating products such as heads of magnetic recording, memories, nanoelectrodes, sensors etc. These advanced applications were possible to be realized through two parallel procedures. On the one hand, the continuous improvement in photolithography has made possible decrease at submicrometric level of dimensions. On the other hand, theoretical understanding of microelectrochemical engineering principles has been developed very much, including an explanation of current distribution, mass transport, electrode kinetics and nucleation, as well as growing of microcrystals. All these developments favor and improve the safety of processes in electrochemistry, a fact which allows their implementation on a large scale automated production.

The LIGA technology uses X-ray or UV lithography to create a precision mold. Its name is an acronym from German words: *Litographie*, *Galvanoformung* (electrochemical deposition or electroforming) and *Abformung* (hot plastic deformation) and this technology is applied for fabrication of miniature devices, but with a high aspect ratio. The obtaining of micromechanical structures by LIGA technology involves a substrate (support) that is filed with a photoresist having constant thickness; the photoresist is exposed, is heat treated, developed and selectively removed [17,18]. Basic steps during the fabrication process using LIGA technology are:

-exposure, a step which transfer the design by using a direct write laser lithography system, on a plate coated with photoresist;

-developing step, in which unexposed photoresist is removed chemically; as negative photoresist (unexposed) SU8 type is used, whereas for the exposed (positive photoresist) – AZ type is used;

- metal electrodeposition, when spaces from which the photoresist was removed are "filled " with a metal layer;

- removal of the remaining photoresist and separation of microstructure from the substrate.

The substrate (support) is the electrode on which the electrochemical deposition takes place. Because the LIGA technology took many procedures from microelectronic technology, the substrat is often a semiconductor. As literature shows, until now a number of metals (Ni, especially) and alloys (Ni-Co, Ni-Fe, Ni-P, Ni-W, Ni-Mn, Fe-Co and Au-Cd-As) have been deposited using LIGA procedure. For microstructures, usually the thickness of electrodeposited layer exceeds 10 μm and can reach 1 mm or more in the case of electroforming. However, due to internal stresses that may occur in the layer, nickel is preferentially used to form microstructures. The reasons for the widespread use of Ni layers electrodeposition are their advantageous properties such as color, hardness, corrosive resistance, ductility, leveling, resistance to abrasion, their function as a diffusion barrier and easy bath maintenance of the nickel electrolyte.

The operating parameters in LIGA technology that must be controlled are divided in two categories: (i) parameters involved in achieving the metal deposition: bath parameters (electrolyte, precursor concentration, buffer,

* *Tel.: 0765870791*

additives, *p*H) and temperature; (ii) parameters affecting the uniformity, structure and texture of deposit: current density and application of various current pulses, geometry and configuration of the substrate, stirring of solution.

This paper presents the results of nickel electrochemical deposition on the silicon wafers using LIGA technology, in order to achieve microstructures (including movable microstructures) for micro-mechanical systems. After a selection of optimal conditions for obtaining good quality deposits we made a detailed characterization of obtained Ni layers.

Experimental part

Figure 1 shows a scheme during the fabrication of electroplated 3D microstructures. For these experiments the support consisted in commercial n-type (100) Si wafers with 10 cm diameter and 525µm thickness; the support is indicated as (1) in figure 1. As a pre-treatment, the silicon surface was covered with a SiO_2 film (500 nm) and a Cr/Au layer (denoted (2) in fig. 1), on which either SU8 50 or SU8 100 types photoresist (Microresist Technology, Germany, denoted (3) in fig. 1) having 100µm, 200µm or 400µm thicknesses was applied. During the photolitography steps, the routes of non-exposed photoresist were developed with an organic solvent, 1-methoxy-2-propyl-acetate, commercially named mr-Dev 600 reagent (Microresist Technology). Nickel layer (4) was then electroplated on these routes. Finally, the remaining photoresist was removed using organic solvent (developing step) and the obtained nickel structure was detached from the substrate (2). This last operation step of the microstructures separation was carried out using a hot 50% KOH aqueous solution (50-90^{0}C), when SiO_2 film and Si (100) wafer are chemically dissolved. Because the dissolution rate of SiO_2 and Si is lower at 50^{0}C, the operation was performed at 90^{0}C, with 1.45 nm/min dissolving rate.

It is worth to mention that in another series of experiments we obtained successfully the same microstructures by changing the nature of substrate, *i.e.* using either 316L stainless steel (Otelinox, Romania) or ITO glass (Diamond Coatings, Great Britain), confirming the results of previous works [19,20] that have used SU8 2050 photoresist during the same LIGA procedure for obtaining micro-mechanical structures.

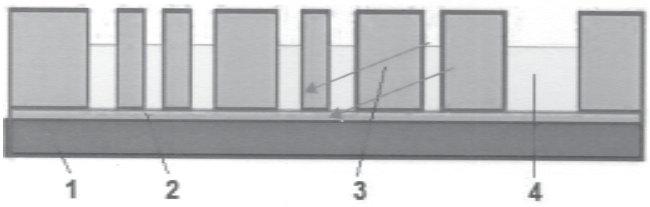

Fig. 1 Scheme of processing assembly: Si wafer (1), SiO_2 film on which a Cr/Au film was superposed (2), portions of SU8 photoresist still non-developed (3) and non-detached micro-mechanical system composed of Ni deposit (4).

Our preliminary experiments of electrolysis were carried out comparatively using Watts bath or nickel sulfamate based electrolytes. The sulfamate $Ni(NH_2SO_3)_2$ bath was selected as more appropriate for association with LIGA technique owing to its better throwing power, covering power and reproducibility; also, the use of sulfamate electrolyte allows to deposit Ni layers with higher hardness (of maximum 400 HV comparative to 200 HV for Watts bath). The following optimal electrolyte composition was chosen: 300 gL^{-1} $Ni(NH_2SO_3)_2$, 30 gL^{-1} $NiCl_2.6H_2O$, 30 gL^{-1} H_3BO_3, 7.5 gL^{-1} naphtalene tri-sulfonic acid and 0.05-0.1 gL^{-1} sodium lauryl sulphate. *p*H values (measured using a Inolab electrometric pH-meter) were kept within 3.5-4.2 range with amidosulfonic acid as additive. All reagents were purchased from Merck.

The operating conditions for preparing Ni microstructures were the following: current densities in the 2-5Adm^{-2} range, 2-5V voltage and electrolyte temperatures in the range of 50-55^{0}C. A two-electrode cell [21] was used containing the support, processed as above described, as cathode and a Ni plate with large area as anode. The Ni deposition runs are followed by rinsing with running water and distilled water and drying, as usually. A magnetic stirring of electrolyte was performed for avoiding diffusive control of mass transfer at cathode and for working with an increased current density.

The Ni layer thickness was determined gravimetrically knowing the density of pure Ni $\rho_{Ni}=8.908 gcm^{-3}$ and estimating the surface area of Ni deposit. The current efficiency involved in the cathodic process was evaluated by weighing deposited mass and taking into account the Faraday's law, by using the number of transferred electrons z=2.

Images of Ni deposits were obtained using a Stemi 2000-C (Carl Zeiss) optical microscope with Axio camera and a FESEM-FIB Auriga (Carl Zeiss) SEM microscope. X-ray diffractometry measurements (XRD) were carried out using Bruker AXS D8 ADVANCE diffractometer with Cu anode and k_β Ni filter. For hardness examination a Vickers FM 700 type, XMO 195, equipment was employed together with a MP NRW 173430.1007 sample as a hardness etalon.

Results and discussion

Table 1 shows a first characterization of Ni layers with thicknesses between 30 and 180 µm, obtained at current densities in the range 2.5-5 Adm^{-2} and electrolysis duration

No.	Temperature, ^{0}C	Current density, A/dm^2	Time, min.	Layer thickness, µm	Deposit appearence
1	52-55	3.5	60	30-40	Bright uniform deposit, well shaped (with distinct borders, Fig.2)
2	52-55	2.6	180	70-80	Deposit with glossy and uniform central part, but with dull and dendritic edge portions (Fig.3)
3	52-55	5	180	90-100	Deposit with bright uniform central part, but dendritic edge portions (Fig.4,5)
4	52-55	3	210	110-120	Uniform deposit in shape of miniaturized gears, with some dendrites on the contour of gears (Fig. 6)
5	52-55	2,5	300	160-180	A weak uniformity of deposit, satisfactory in central part, only; promient dendrites on the edges

Table 1
OPERATION CONDITIONS AND APPEARANCES OF NICKEL DEPOSITS OBTAINED USING SULFAMATE BATH

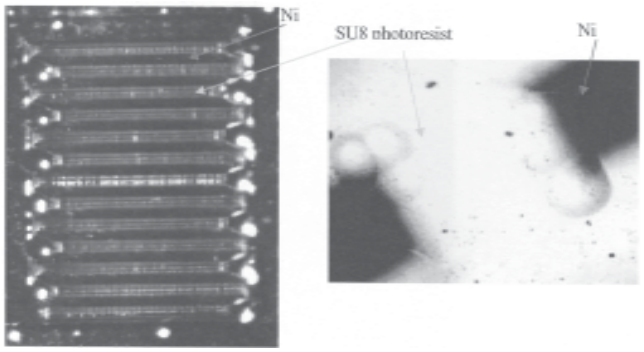

Fig. 2 Optical image of a network with beams (a) having 30μ Ni layer thickness and a micrography (b) at x50 magnification.

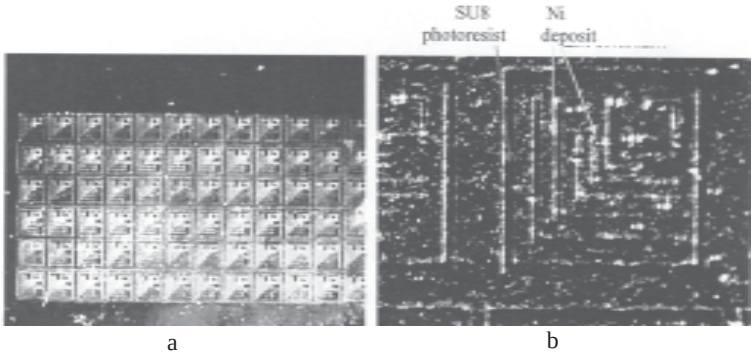

Fig. 3 Optical image of a network of microsquares (a) with 80μ Ni layer thickness and a image detail (b) at x50 magnification.

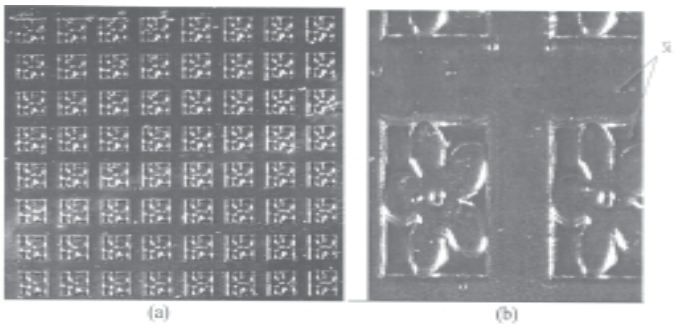

Fig. 4 Optical image of a network of microflowers (a) with 100μ Ni layer thickness and a image detail (b) at x50 magnification.

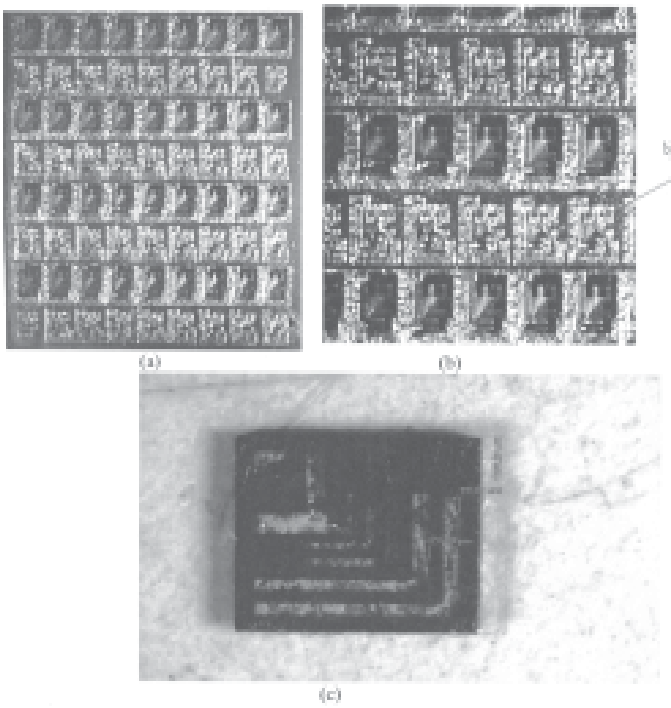

Fig. 5 Optical images of another network of microsquares (a,b) with 80-100μm Ni layer thickness and a image detail (c) at x50 magnification, where the layer thicknesses of 73.89 μm or 99.02 μm were indicated locally.

between 1 and 5 h. Values of 98-99% current efficiencies were determined gravimetrically. The appearances of obtained Ni layers were presented in table 1 together with operating conditions.

Figures 2-6 show optical images of networks, on the whole and details, and confirm the appearance of uniform and smooth deposited Ni layers. Figure 2 presents an example of network in a shape of microbeams deposited on a support having 100μm photoresist. For the 30μm thick Ni layer, a clear delimitation of the edges is noticed and the lack of any dendrite, too; this is a result of a very high throwing power of sulfamate bath, which is very useful for complex shapes of electroplated objects. Also, a very uniform deposit is illustrated in figure 3 for a thicker Ni layer (around 80μm), especially for the central part of each microsquare; however, some dendrites are observed on the edges (in the detail).

Figures 4 and 5 show optical images of prepared microflowers and microsquares, but having a higher layer thickness, up to 100μm. The same bright and smooth Ni deposit was obtained on the most of surface in all cases; however, numerous and more prominent dendrites as well as a quite rough surface are now observed on the edges, due to the longer electrolysis time. There are remarked some differences in local thickness (73.89μm or 99.02μm in the two points, shown by fig. 5c), which may indicate differences in the deep of penetration of electroplating solution (sulfamate solution) in spite of its good throwing power.

Figures 6 a-d present sequences during the fabrication of movable parts of a micro-mechanical system, namely

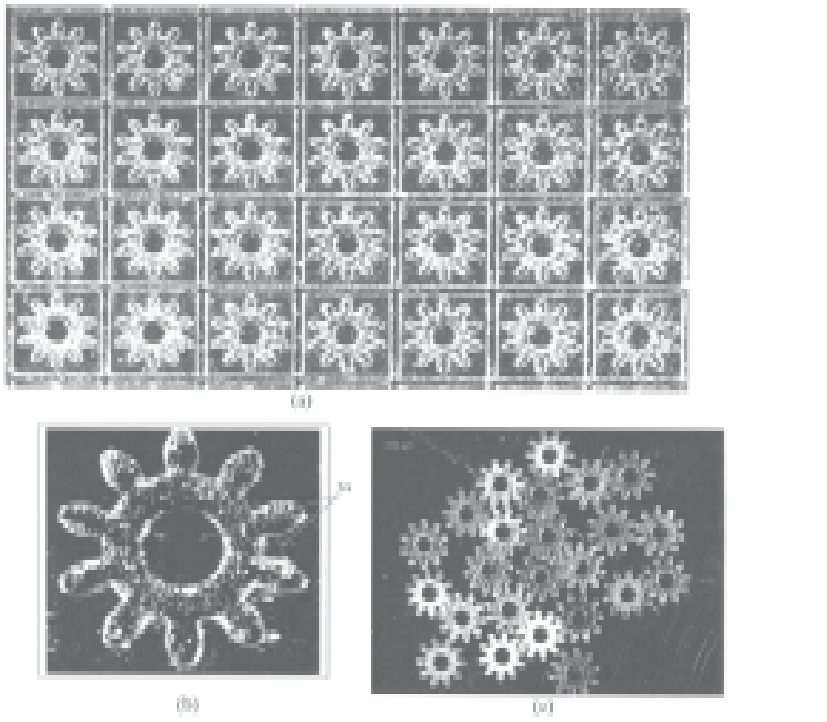

Fig. 6 Optical image of a network of microgears (a) with 120μm Ni layer thickness, a image of a single gear (b) at x50 magnification, a image at x10 magnification of several gears detached from the silicon wafer substrat (c) using a hot 50% KOH solution at 90^0C and a gear couple (d) at x32 magnification

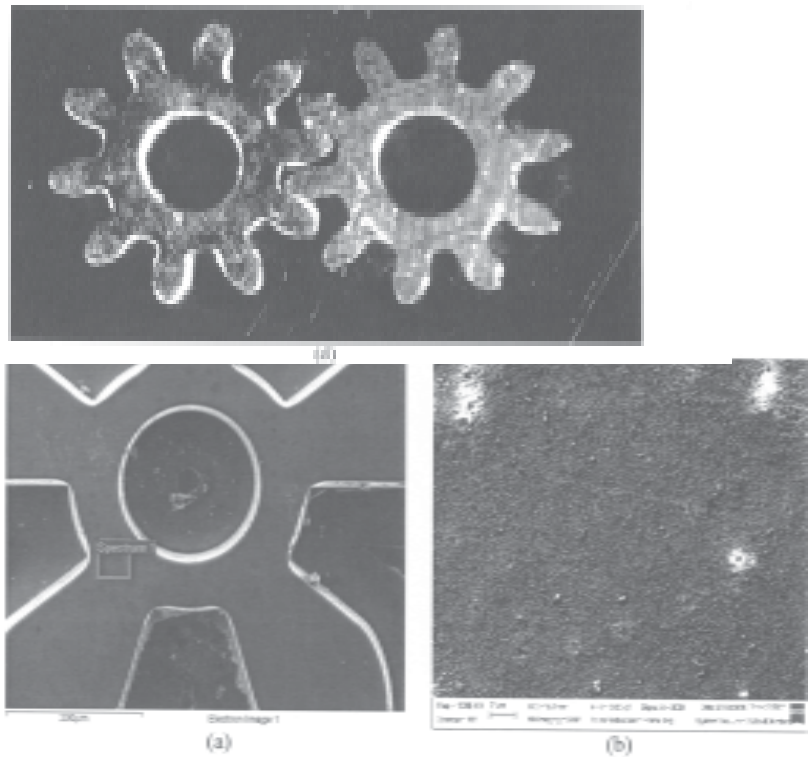

Fig. 7 SEM micrograph (a) for a single microgear; SEM image at x10000 magnification for the zone indicated in figure 7a

microgears. Nickel layers of 110-120 μm thickness were obtained after the electrodeposition step, and their appearance is also of good quality (bright, smooth, uniform) leading to well shaped microgears, especially in the central zone of figure 6a. Some rough deposit and dendrites are noticed on the edge zone of the main substrate, as well as imperfections consisting of remaining resist in the space between wheel teeth may be observed in the detailed images of separated microgears.

It is worth to mention that the aspect of Ni deposits having the highest thickness (160–180 μm) indicates a weak uniformity of deposit, in general being satisfactory only in central part of deposition place. More prominent dendrites are grown on the surface of borders.

A characterization of morphology is presented by SEM micrographs, an example is given in figures 7. As the SEM picture (fig. 7b) shows, a coherent Ni deposit with a compact structure is obtained by electroplating procedure, confirming the findings obtained by optical micrographs. This good quality structure with almost equal dimensions of the nickel particles indicates the important role as wetting and brightener agents of additives introduced in sulfamate bath, namely naphtalene tri-sulfonic acid and sodium lauryl sulphate, as well as the selection of their appropriate concentration.

Also, a relatively high purity of deposited Ni may be considered from information provided by EDX spectrum (fig. 8). From table 2 that shows the results of the elemental chemical analysis it result a impurity level of less than 3 wt.%, which is a reasonable layer purity from technical point of view. A content of 0.43 wt.% sulphur is always expected during nickel electrodeposition in sulfamate bath, because the products of decomposition of sulfamate anions may be incorporated in the deposit. Also, the

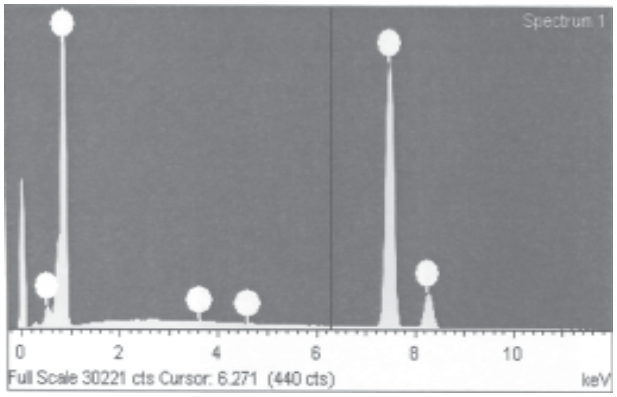

Fig. 8 EDX spectrum for chemical analysis of elements in the zone indicated in figure 7a

Table 2
RESULTS OF EDX CHEMICAL ANALYSIS OF NICKEL DEPOSIT (ZONE INDICATED IN FIG. 5)

Element	Weight%	Atomic%
O (K)	2.42	8.36
Ni (K)	97.15	91.44
S (L)	0.43	0.20
Total	100.00	100.00

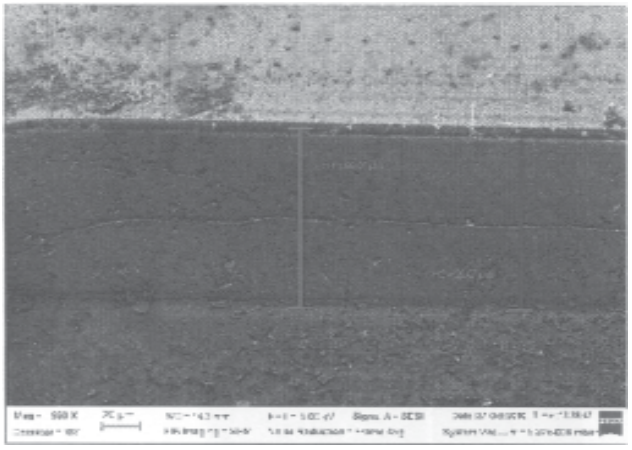

Fig. 9 SEM micrograph at x930 magnification for a cross-section in a microgear, evidencing the uniform thickness of Ni layer (99.07 μm exactly) between substrate and insulator coverage

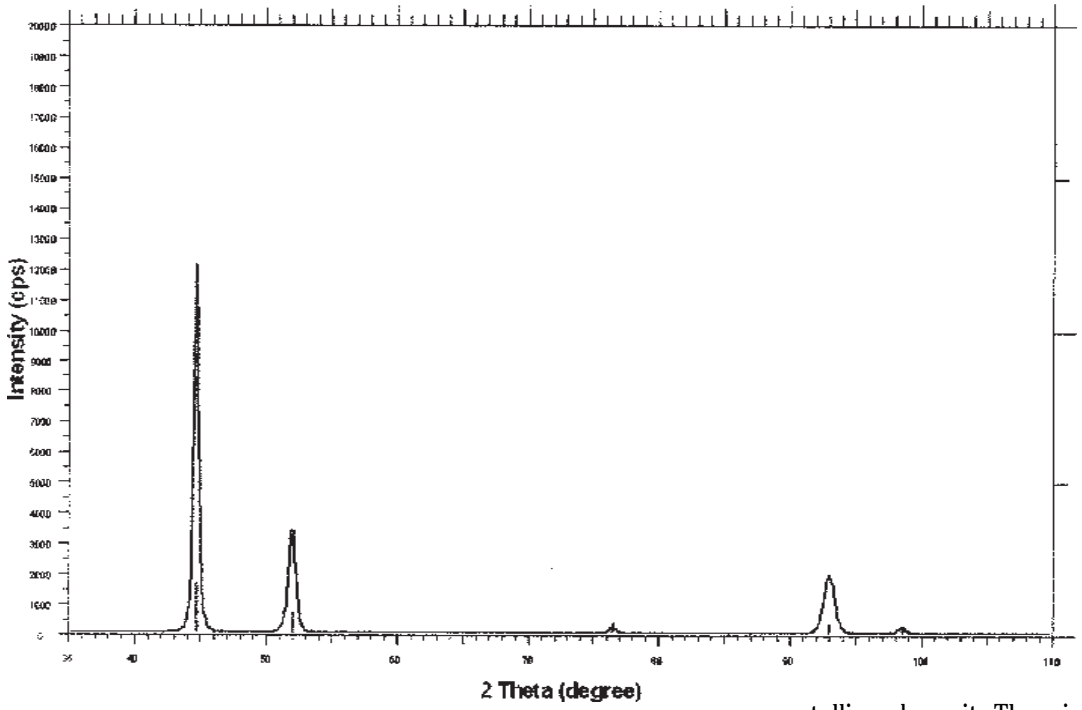

Fig. 10 RDX spectrum for a sample of Ni layer deposited on Si wafer using sulfamate bath.

2.42 wt.% percentage of oxygen indicates some amounts of nickel oxide and/or sulphur oxides, an effect which is more plausible to take place in such operating conditions (around 50^{0}C temperature).

As figure 9 shows, a cross-sectional view in a nickel layer (a microgear section is presented in this figure) illustrates an exactly thickness of the deposit, a 99.07μm dimension being measured in two different places.

XRD spectra were recorded to get information on the deposit structure. An example of results obtained by X-ray diffraction measurements is presented in figure 10. The shape of this spectrum with narrow peaks suggests a very crystalline deposit. The nickel phase has electro-crystallised in *fcc* (face centered cubic) crystallographic system, as resulted by identification of Ni samples with indexing code number 00-004-0850 (ICDD data base). The collection of main peaks consists mainly in five characteristic peaks: three of them, at 2q = 45^0, 52^0 and 77^0 were attributed to Ni species and the other two peaks (at 93^0 and 98^0) may be attributed to nickel oxide.

By processing the XRD data, the average size of crystallites was calculated using the Debye-Scherrer equation:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

Table 3
CRYSTALLOGRAPHIC PARAMETERS OF ELEMENTARY CELL AND CRISTALLITE DIMENSIONS OF NICKEL DEPOSITS

System of Ni crystalline phase	Crystallographic plane (hkl)	Interplanar distance d (Å)		Parameters of elementary cell a (Å)		Mean value of crystal dimension, D_{hkl} (nm)
		theoretical	experimental	theoretical	experimental	
Face centered cubic (fcc)	(1 1 1)	2.03400	2.03376	3.521	3.522	19.56
	(2 0 0)	1.76200	1.76169			13.57

Table 4
VICKERS MICROHARDNESS VALUES ($kgfmm^{-1}$) OF NICKEL DEPOSITS

Sample	Individual value of HV 0.025/15, H1...5, $kgmm^{-2}$	Mean value of HV 0.025/15, $\overline{H}$
Ni microgear	334	**333.6** $kgmm^{-2}$ **(3.336** GPa) (arithmetical mean value)
	327	
	327	
	346	
	334	

where D is grain size, λ is the wavelength of the X-rays, λ=0.154056nm in our case; B is the full width at half maximum (FWHM) and θ is the half diffraction angle of crystal orientation peak. Table 3 contains the obtained structural data, including the parameters of elementary cell. The crystallite size ranges from 13nm to 19nm.

The characterization of mechanical properties of nickel layers was performed by determination of Vickers microhardness (HV). The indentation tests were performed with a constant load of 0.025kgf, at 15 s time duration, 23.5^{0}C temperature and 27% relative air humidity.

The results of HV measurements for surface of Ni micromechanical systems are presented in table 4. In this Table, the individual hardness values, H1...H5 (on different sites on the indentation area) are listed together with the arithmetical mean value. However, it may be noted that for the majority of samples, these values of Vickers hardness for Ni deposit are slightly lower, comparatively to those of samples with large areas (nickel plates, for instance), that may have even a hardness of about 500 $kgf.mm^{-2}$ (5 GPa), as literature reports [22].

Conclusions

The use of a nickel sulfamate bath possessing the required good throwing power, buffer capacity and stability for the electrodeposition of nanocrystalline and smooth Ni is proposed. The experiments carried out allowed the obtaining of nickel layers of different thicknesses on silicon wafers as supports using LIGA litography procedure. Afterwards, the preparation of micro-mecanical systems in different shapes and dimensions was successfully achieved by etching the silicon support with hot concentrated KOH solution. A selection of optimum operating conditions was also done.

Better appearance was for relatively thin nickel layers; they are uniform and in general fine-grained and mirror-bright. The nanometric crystallite size was evidenced by optical and SEM microscopy, as well as by XRD spectra. A relatively high Vickers microhardness (around 330-340 $kgf.mm^{-2}$ or 3.3 - 3.4 GPa) was also measured.

For micro-mechanical systems consisted of thicker nickel layers (90-100μm or more) the same characteristic appearance was noticed, especially in the central zone of support mold; however, dendrites and dull or rough surface portions are observed on the edge zones. An alternative to overcome this shortcoming is the introduction of supplementary additives in the bath solution (to release the internal stresses of Ni electrodeposit) and application of current pulses during electrolysis.

References

1. DATTA, M., LANDOLT, D., Electrochim. Acta, **45**, 2000, p. 2535.
2. KOLLIA, C., SPYRELLIS, N. AMBLARD, J., FROMENT, M., MAURIN, G., J. Appl. Electrochem., **20**, 1990, p. 1025
3. MACHERAS, J., VOUROS, D., KOLLIA, C., SPYRELLIS, N., Trans. Inst. Met. Finish., **74** (2), 1996, p. 55
4. BANOVIC, S.W., BARMAK, K., MARDER, J., Mater. Sci., **33**, 1998, p. 639
5. ARGYRIOU, A., SPYRELLIS, N., Trans. Inst. Met. Finish., **71** (3), 1993, p. 83.
6. WEIL, R., Annu. Rev. Mater. Sci., **19**, 1989, p. 165
7. GOU, S.P., SUN, I.W., Electrochim. Acta, **53**, 2008, p. 2538
8. KIM, I., WEIL, R., Thin Solid Films, **169** (1), 1989, p. 35
9. VASILACHE, V., GUTT, G., VASILACHE, T., Rev. Chim.(Bucharest), **59**, no. 8, 2008, p. 915
10. VASILACHE, V., GUTT, G., VASILACHE, T., Rev. Chim.(Bucharest), **59**, no. 9, 2008, p. 1005
11.VASILACHE, V., GUTT, G., VASILACHE, T., SANDU, I., Rev. Chim.(Bucharest), **60**, no. 1, 2009, p. 15
12. FLOREA, A., ANICAI, L., COSTOVICI, S., GOLGOVICI, F., VISAN,T., Surf. Interface Anal., **42,** 2010, p. 1271
13. WINAND, R., Electrochim. Acta, **39**, 1994, p. 1091
14. BUDEVSKI, E. STAIKOV, G. LORENZ, W.J., Electrochim. Acta, **45**, 2000, p. 2559
15. OETTEL, H. KLIMANEK, P., Mat. Sci. Forum, **273–275**, 1998, p. 55.
16. FRITZ, T., MOKWA, W., SCHNAKENBER, U., Electrochim. Acta, 47 (2001) p. 55
17. SCHULZ, J., Study concerning metal microstructure processing using LIGA technology, Report, Microworks Company, Karlsruhe, 2008, p. 21-33, 38-43
18. KOCH, C., RINKE, T.J., Lithography – Theory and Application of Photoresists, Developers, Solvent and Etchants, MicroChemicals Company Manual, 2008, p. 31-52, 55-67
19. *** NANO SU8 – Negative Tone Photoresist Formulation 50-100, MicroChemicals company's catalog, 2002
20. *** SU-8 2000– Permanent Epoxy Negative Photoresist. Processing Guidelines for: SU-8 2025, SU-8 2050 and SU-8 2075, MicroChemicals company's catalog, 2002
21. PRIOTEASA, P., GOLGOVICI, F., SBIRCEA, G., ANICAI, L., VISAN, T., Rev. Chim. (Bucharest), **61**, no. 11, 2010, p. 1046-1053
22. GRUNWALD, E., MURESAN, L., VERMESAN, G., VERMESAN, H., CULIC, A., Tratat de galvanotehnica, Casa Cartii de Stiinta, Cluj-Napoca, 2005

Manuscript received: 28.02.2011