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 components, micro-electro-mechanical systems (MEMS). On the other hand, the continuous improvement of micromechanical systems were possible to be realized through two parallel nanoelectrodes, sensors etc. These advanced applications as heads of magnetic recording, memories, photonics, thermoelectronics, to creating products such as antennas, micro motors, diodes, lasers, solar cells, or high frequency and high precision microstructures, sensors and actuators [13-16]; some examples are: nanoelectronics, photonics, thermoelectronics, to creating products such as heads of magnetic recording, memories, photonics, thermoelectronics, to creating products such as antennas, micro motors, diodes, lasers, solar cells, or high frequency and high precision microstructures, sensors and actuators [13-16].

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 filled with a photoset having constant thickness; the photoset 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 photoset;
- developing step, in which unexposed photoset is removed chemically; as negative photoset (unexposed) SU8 type is used, whereas for the exposed (positive photoset) – AZ type is used;
- metal electrodeposition, when spaces from which the photoset was removed are “filled” with a metal layer;
- removal of the remaining photoset and separation of microstructure from the substrate.

The substrate (support) is the electrode on which the electrochemical deposition takes place. Because the LIGA technology takes 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,
additives, pH) 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 SiO2 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 photolithography 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 aqueous solution (50-90°C), when SiO2 film and Si (100) wafer are chemically dissolved. Because the dissolution rate of SiO2 and Si is lower at 50°C, the operation was performed at 90°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.

Our preliminary experiments of electrolysis were carried out comparatively using Watts bath or nickel sulfamate based electrolytes. The sulfamate Ni(NH₂SO₃)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(NH₂SO₃)₂, 30 gL⁻¹ NiCl₂.6H₂O, 30 gL⁻¹ H₃BO₃, 7.5 gL⁻¹ naphtalene tri-sulfonic acid and 0.05-0.1 gL⁻¹ sodium lauryl sulphate. pH 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 30-55°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 ρ=8.908g/cm³ 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 Axiò 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 k0 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

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature, °C</th>
<th>Current density, A/cm²</th>
<th>Time, min.</th>
<th>Layer thickness, μm</th>
<th>Deposit appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>52-55</td>
<td>5.5</td>
<td>60</td>
<td>30-40</td>
<td>Bright uniform deposit, well shaped (with distinct borders, Fig.2)</td>
</tr>
<tr>
<td>2</td>
<td>52-55</td>
<td>2.6</td>
<td>180</td>
<td>70-80</td>
<td>Deposit with glossy and uniform central part, but with dull and dendritic edge portions (Fig.3)</td>
</tr>
<tr>
<td>3</td>
<td>52-55</td>
<td>5</td>
<td>180</td>
<td>90-100</td>
<td>Deposit with bright uniform central part, but dendritic edge portions (Fig.4)</td>
</tr>
<tr>
<td>4</td>
<td>52-55</td>
<td>3.5</td>
<td>210</td>
<td>110-120</td>
<td>Uniform deposit in shape of miniaturized gears, with some dendrites on the contour of gears (Fig.6)</td>
</tr>
<tr>
<td>5</td>
<td>52-55</td>
<td>2.5</td>
<td>300</td>
<td>160-180</td>
<td>A weak uniformity of deposit, satisfactory in central part, only; prominent dendrites on the edges</td>
</tr>
</tbody>
</table>

Table 1

OPERATION CONDITIONS AND APPEARANCES OF NICKEL DEPOSITS OBTAINED USING SULFAMATE BATH

Fig. 1 Scheme of processing assembly: Si wafer (1), SiO₂ film on which a Cu/Au film was superposed (2), portions of SU8 photoresist still non-developed (3) and non-detached micro-mechanical system composed of Ni deposit (4).
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 120 μm 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°C and a gear couple (d) at x32 magnification.

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
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 500°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 99.07 μm 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 2θ = 45°, 52° and 77° were attributed to Ni species and the other two peaks (at 93° and 98°) may be attributed to nickel oxide.

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

$$ D = \frac{0.9 \lambda}{B \cos \theta} \tag{1} $$

### Table 2

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O (K)</td>
<td>2.42</td>
<td>8.36</td>
</tr>
<tr>
<td>Ni (K)</td>
<td>97.15</td>
<td>91.44</td>
</tr>
<tr>
<td>S (L)</td>
<td>0.43</td>
<td>2.20</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
<td><strong>100.00</strong></td>
</tr>
</tbody>
</table>

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

Fig. 9 SEM micrograph at x300 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 sulamate bath.
where D is grain size, $\lambda$ is the wavelength of the X-rays, $\lambda = 0.154056 \text{nm}$ in our case; B is the full width at half maximum (FWHM) and $\theta$ is the half diffraction angle of crystal orientation peak. Table 3 contains the obtained structural data, including the parameters of elementary crystal orientation peak. Table 4 contains the obtained supplementary additives in the bath solution (to release over this shortcoming is the introduction of dendrites and dull or rough surface appearance was noticed, especially in the central zone of the sample. An alternative to support mold; however, 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$^{-2}$) was also measured.

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 0.025 kgf, at 15 s time duration, 23.5°C temperature and 27% relative air humidity. The results of HV measurements for surface of Ni micro-mechanical systems are presented in Table 4. In this Table, the individual hardness values, $H_1...H_5$ (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 lithography 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**

19. *** NANO SU8 – Negative Tone Photoresist Formulation 50-100, MicroChemicals company’s catalog, 2002

**Table 3**

<table>
<thead>
<tr>
<th>System of Ni crystalline phase</th>
<th>Crystallographic plane (hkl)</th>
<th>Interplanar distance d (Å)</th>
<th>Parameters of elementary cell</th>
<th>Mean value of crystal dimension, $D_{\lambda_{0}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face centered cubic (fcc)</td>
<td>(1 1 1)</td>
<td>2.03400</td>
<td>2.03376</td>
<td>3.521</td>
</tr>
<tr>
<td></td>
<td>(2 0 0)</td>
<td>1.76200</td>
<td>1.76169</td>
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**Table 4**

<table>
<thead>
<tr>
<th>Ni microgear</th>
<th>Individual value of HV</th>
<th>Mean value of HV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.025/15, H1...H5, kgf.mm$^{-2}$</td>
<td>333.6 kgf.mm$^{-2}$ (3.336 GPa)</td>
</tr>
<tr>
<td>234</td>
<td></td>
<td>(arithmetical mean value)</td>
</tr>
<tr>
<td>227</td>
<td></td>
<td></td>
</tr>
<tr>
<td>327</td>
<td></td>
<td></td>
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