This paper presents the development of nickel phosphorus (Ni-P) micromolding for the manufacturing of a 3D electrostatic energy harvesting microsystem. Ni-P alloy exhibits weak ferromagnetic properties beyond 10–12 wt% phosphorus content. Deposits were prepared at different current densities (−10 to −150 mA/cm²) and concentration of phosphorus acid in the electrolyte (0–20 g/l). It was found that the deposition rate decreases when phosphorus content increases in the deposit. The final process leaded the choice of a H₃PO₃ concentration of 5 g/l to reach a 0.1 μm/min deposition rate for phosphorus content higher than 13 wt%. Mechanical, electrical and magnetic properties of the Ni-P films were investigated on 1 mm² and 1 cm² square deposit and confirmed the suitability of that material for the target MEMS. Comb patterns of micromolded Ni-P have been realized on a 2-inch wafer, leading to a 10 μm thick deposit containing 13.5 wt% in P, which is, at our knowledge, the first high phosphorus Ni-P micromolding involving electrodeposition growth for 3D MEMS applications.

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The latest generation of pacemaker, lead-free, is directly implanted in the cardiac cavities of the heart, thus improving considerably patient comfort and reducing complications with common pacemaker such as lead failure. However, leadless pacemakers should overcome several issues such as the limited lifespan of the lithium-based battery used to supply those pacemakers. This involves a surgery of the patient every 7 to 10 years, whereas about 45% of patients survive more than 10 years after their first pacemaker implantation. The challenge for improving pacemaker’s lifetime explains the strong interest for harvesting energy from the heart, which is a long reliable energy source.

Among the solution leading to a volume compatible with implantation in the heart by intravenous catheter, energy harvesting from inertial movement seems promising once its design challenges the very low fundamental heart beat frequencies (1–3 Hz). Our team has already proposed such a design for an out-of-plane overlap electrostatic energy harvesting MEMS that would be able to harvest about 10 μW in average power. The final layout of the proposed device is presented in Figure 1. The device is 5.5 mm in diameter and will have a total height of 1 mm.

The fabrication process of such device is compatible with other types of 3D MEMS and is based on an original additive process (Figure 2) combining alternative electroplating of a patterned structural material (nickel) and a sacrificial material (copper). Nickel and copper have been chosen respectively for their mechanical properties, their high growth rate and the high etching selectivity of copper against nickel during wet etching. Electroplating is a low cost, fast and simple fabrication process which makes it very suitable for thick film growth. When combined with a lithography step in the micromolding process, film patterning is achieved (Figure 2a) by localized growth inside the mold. Finally the process is completed by a sacrificial layer growth (Figure 2b) and planarization (Figure 2c) which allows numerous repetitions of the structural material micromolding (Figure 2d) with different pattern designs. After a selective etching of the sacrificial layer, the final 3D structure is revealed and released (Figure 2e). A SEM view of a recently fabricated nickel prototype of the electrostatic energy harvester is presented in Figure 3. This structure is composed of ten layers of nickel (three layers of springs, three layers of fingers, three inter-layer and one support layer) of 20 μm each. Hence, the first prototype has a total height of 200 μm.

Figure 1. Layout of the device. CAD view (left) and layout of the 4 different types of layers (right).

Another issue of implanted pacemakers is the lack of full body Magnetic Resonance Imaging (MRI) compatibility which could be seen as a real problem for medical diagnostic. Indeed, 75% of patients worldwide with implanted cardiac devices will probably need...
an MRI scan during the lifetime of their device. However, in 2014, the first pacemaker with full body MRI compatibility has been proposed by Medtronic. To be fully seen as an improvement in all aspects, leadless pacemaker would need to be also MRI compatible. For this purpose, ferromagnetic materials, which could be patternable with several microfabrication techniques, should be avoided because the strong permanent magnetic field used for MRI could induce the dislodgement of the implant. Moreover, the presence of metals could lead to the heating of skin tissues during MRI because of Eddy currents.

The design of a MRI-compatible heart implanted pacemaker, small in volume, without a lead system and autonomous, is possible by the integration of non-ferromagnetic material. This motivated the development of Ni-P micromolding. Indeed, magnetic properties of Ni-P alloy depends on phosphorus content in the material and for content higher than 10–12 wt%, the magnetization is very low (less than 2 emu/g), while keeping mechanical properties closed to those of pure nickel.

In this paper, we first present the optimization of working conditions for Ni-P micromolding, then the realization of Ni-P micropatterns related to the 3D electrostatic energy harvesting microsystem.

Experimental

Substrate preparation for Ni-P electroplating deposition.—Substrates were (100) oriented and wet oxidized (100 nm SiO₂) silicon wafers (2-inch diameter, 280 μm thickness). The micromolding process, consisting in two main steps (lithography and electrodeposition), has already been described and begins with the realization of a photoresist mold by photolithography (Double-side EVG 620 mask aligner) on a metallic seed layer (Ti 10 nm/Cu 100 nm) previously sputtered (Denton Vacuum Sputtering System-Explorer14) on the substrate. The photoresist mold consisted in an array of 1 mm² or 2 μm² square apertures. MicroChemicals AZ4562 has been spincasted for different thicknesses (7 μm, 20 μm or 35 μm). Just before electrodeposition, a pre-treatment by O₂ plasma (Diener Electronics, Pico A version) is performed in order to improve electrophilic properties of the photoresist.

Electrolyte preparation.—The aqueous electrolytic bath consisted of nickel sulfate, nickel chloride, phosphorous acid, respectively as nickel and phosphorus sources, and boric acid as buffer and electrolyte support. It was prepared by adding the appropriate amounts of laboratory grade chemicals to deionized water at room temperature. Magnetic stirring was then carried out until salt dissolution is completed. Electrolyte concentrations are presented in Table I. At first, saccharine was used as an additive, but baths were instable at room temperature (precipitation occurred) which challenged deposit repeatability. In order to compare the properties of Ni-P to pure Ni, a common Watts electrolyte has also been made with the same amount of nickel sulfate, nickel chloride and boric acid.

Electrodeposition.—Electroplating was carried out in a 500 ml beaker. A nickel plate was used as the soluble anode. The inter-electrode distance was kept constant to 2 cm. The continuous current was injected using a potentiostat (Metrohm, AUTOLAB PGSTAT302N, I_max = 2 A). Several plating parameters were tested including temperature (21°C or 50°C) and agitation (magnetic stirring). Bath temperature and magnetic stirring were controlled with a digital heating bath (IKA HBR4 Digital, IKA-WERKE). After deposition, the sample was immediately removed from the solution, rinsed with deionized water and dried with nitrogen.

To identify working conditions enabling thick deposits with high phosphorus content, the current density was varied from −10 to −150 mA/cm² and the deposition time ranged from 15 min to 2 h. The plating conditions are presented in Table II. The pH of the solutions was between 1 and 2, slightly decreasing with the increase of H₃PO₄ concentration.

Characterization of deposits.—All the films were characterized as-deposited, the common thermal treatment, involving temperature being not compatible with the overall targeted process. Furthermore, thermal treatment leads to crystal phase change and grain growth. In the case or Ni-P alloy, magnetic properties are improved, what is detrimental to the aimed application. After dissolution of the photoresist in acetone, the surface morphology was characterized by optical microscopy (Olympus BX60) and Scanning Electron Microscopy (SEM, Hitachi 3600N). The samples composition was analyzed with an energy-dispersive spectrometer (EDS) SEM accessory (ThermoNoran System SIX). Nickel and phosphorus elements have been quantified using the K peaks with a 15 keV electron beam. The thickness of the deposits was measured using an optical interferometer (Dektak 8, Veeco). From these measurements, the roughness has been estimated. The deposits resistivity has been deduced from 4-point collinear probe method (Lucas lab probes and Keithley current source and voltmeter). Micro-indentation characterization was also carried out to estimate Young’s modulus and hardness of deposits. All micro-indentations were performed with the CSM Micro Indenter (MHT) using a diamond Berkovich (triangular pyramidal) tip. The structure of deposits was studied by means of a PANalytical X’Pert PRO equipment using the Cu Kα radiation (λ = 1.5418 Å). Magnetic properties were characterized by means of a Stanford Instrument Alternating Gradient Force Magnetometer (AGFM) at room temperature. Because a large area was needed for electrical, structural and mechanical measurements, these characterizations were carried out on 1 cm² samples whereas magnetic measurements were carried out on 1 mm² samples.

Table I. Composition of the electrolytic bath.

| Concentration (g/l) | Concentration (M) |
|---------------------|------------------|
| NiSO₄, 6H₂O         | 197              | 0.75          |
| NiCl₂, 6H₂O         | 4.7              | 0.02          |
| H₃BO₃              | 24.7             | 0.40          |
| H₃PO₄              | 0–20             | 0–0.24        |

Table II. Plating conditions.

| Magnetic stirring | 250 rpm |
|------------------|---------|
| pH               | 1–2     |
| time             | 15 min–2 h |
| temperature      | 21°C or 50°C |

Figure 3. SEM view of a nickel prototype of the 3D energy harvester.
Results and Discussion

Deposit appearance.—The as-plated Ni-P patterns were characterized by using optical and electronic microscopy. The patterns, with gray color, present a bright metallic appearance in the range of the applied current density. A typical morphology is a layer of densely packed particles with diameter less than 100 nm and a smooth surface (roughness < 10 nm rms).

With the raise of current density (above −100 mA/cm² for the 1 mm² square patterns), delamination occurs during the sample rinsing and drying steps, and even during the electrodeposition for the highest current densities. Delamination was also observed at lower current density (−30 mA/cm²) while the electrolyte is not agitated. It also occurs at lower current density for larger surface to be plated: −30 mA/cm² for the 1 cm² pattern (Figure 4).

Phosphorus content.—Ni-P deposits were prepared at different plating conditions with the 1 mm² patterns. The effect of current density and concentration of phosphorous acid in the bath on the phosphorus content in the deposit were systematically investigated. These contents are extracted from the EDS analysis of the whole surface of one 1 mm² pattern, on which the composition variation is less than 1%.

Electrodeposition realized at room temperature (21 °C) leads to deposits with low phosphorus content, typically lower than 10 wt%. When the bath was agitated and heated to 50 °C, higher contents between 8 and 18.3 wt% have been obtained.

Figure 5 shows the variation of phosphorus content of the deposit as a function of the current density for three different H₃PO₃ concentrations in the electrolytic solution and for a working temperature of 50 °C. At low current density, i.e. −10 mA/cm², phosphorus contents in the deposit are quite the same for the three H₃PO₃ concentrations. For higher current densities, phosphorus content increases while the concentration in H₃PO₃ increases. For instance, at a current density of −50 mA/cm², the phosphorus content is about 10.4, 15.4 and 16.7 wt% for 5, 10 and 20 g/l of H₃PO₃ respectively. The results are consistent with already reported studies.9,10 For the lowest H₃PO₃ concentration, phosphorous contents decrease with the current density. In all cases, plateaus seem to be reached at high current density.

Deposition rate.—Thickness of Ni and Ni-P deposits was also systematically investigated. It varies from 0.2 µm to 20 µm and increases linearly with the plating time. Figure 6 shows deposition rate variation with the current density for the three H₃PO₃ concentrations. The results are also consistent with already reported studies.9 First, the deposition rates increase with the current density for all electrolytes. Second, Ni-P deposition rates are lower than the one of pure Ni and decreases with the addition of H₃PO₃, meaning that the rate decreases when the phosphorous content increases in the deposit. To target high phosphorous content and high deposition rate, a trade-off has to be made.

Electrical characterization.—4-probe measurements allowed estimating the deposit resistivity in the 67–153 Ω·cm range for Ni-P with phosphorus content larger than 12 wt% and in the 7–12 Ω·cm range for pure Ni. In both cases, electrical resistivity is suitable for both electrostatic MEMS application, and for the additive global process in which a layer must be conductive enough to ensure the electrodeposition of another layer above.

Structural information.—Nickel has a face-centered cubic structure. XRD analysis (Figure 7) shows that as-deposited samples with a high phosphorus content (13.8 wt% for the sample analyzed) present an amorphous structure with one broad peak (6° of FWHM) around
45°, i.e. corresponding to the (111) plane of nickel. The amorphous nature of Ni-P alloy suggests weak magnetic properties.15

**Magnetic characterization.**—Magnetic measurements were performed both on pure electrodeposited Ni and Ni-P deposits (Figure 8, Table III). Saturation magnetization of Ni-P samples is less than 100 times the one of nickel. Even if these results are subject to uncertainty due to sample volume estimation, they confirm that high phosphorus content deposits have very low ferromagnetic properties. Several hypotheses could explain the remaining ferromagnetic contribution of the material such as heterogeneity of composition in the first atomic layers or pure nickel inclusion. This result is very promising for MRI safety of nickel-based MEMS regarding the permanent magnetic field inside MRI scanners. Additional measurements should be performed regarding the heating due to the RF gradient fields.

**Mechanical measurements.**—Mechanical properties were extracted using Oliver & Pharr estimation method.16 Young’s modulus and hardness were estimated by carrying five indentations of increasing depth. To remain under conditions of low deformation, the maximum penetration depth of the indenter was 10% of the film thickness. We present in Table IV the comparison between pure nickel and Ni-P. Young’s modulus tends to decrease with the indenter penetration which explains the standard deviation. Both materials exhibit similar mechanical properties which is a promising result for integration of Ni-P in 3D MEMS.

**Ni-P Micromolding of Patterned Combs**

The technological steps are almost the same as those used for the development of the Ni-P electrodeposition process. The main differences are the use of 2 mm thick glass wafer instead of silicon wafer, improving the achievement of the planarization step, and the use of different micromolding patterns. The patterns consist of 50 μm large microfingers separated by a 10 μm gap and which maximum length is 900 μm. In addition, because of thick film delamination when large surface were plated - the overall surface to be plated is high (8.7 cm²) -, we chose (i) to begin the electrodeposition at lower current density (15 min at −5 mA/cm²), this thin layer (less than 400 nm) playing the role of an adhesion layer, (ii) to perform the electrodeposition at −15 mA/cm² (during 1 h). This current density was considered as a good trade-off between deposition rate and phosphorus content. Finally, 10 μm thick micropatterns with an average phosphorus content of 13.5 wt% have been successfully deposited, as shown in Figure 9. Variation in composition between micropatterns is between 12.9 wt% and 13.8 wt%.

### Table III. Magnetic properties extracted from hysteresis cycle.

|                  | Saturation magnetization (mT) | Remanent magnetization (mT) |
|------------------|-------------------------------|-----------------------------|
| Pure Ni          | ≈ 600                         | ≈ 130                       |
| Ni-P (14.6 wt%)  | ≈ 4                           | ≈ 0.7                       |
| Ni-P (18.3 wt%)  | ≈ 1.5                         | ≈ 0.5                       |

### Table IV. Mechanical properties extracted from micro-indentation.

|                  | Thickness (μm) | Young’s Modulus (GPa) | Hardness (GPa) |
|------------------|----------------|-----------------------|----------------|
| Pure Ni          | 7–20           | 145 +/− 15            | 14.2 +/− 1.6   |
| Ni-P (13.8 wt%)  | 9.7            | 141 +/− 31            | 15.7 +/− 3.3   |

**Figure 7.** XRD measurement of a Ni-P (13.8 wt%) deposit.

**Figure 8.** AGFM hysteresis loops for (a) 1.2 μm thick Ni-P (18.3 wt%) deposit and 500 nm thick Ni-P (14.6 wt%) (b) 2.3 μm Ni deposit.

**Figure 9.** Optical (a,b) and SEM (c) observations of the Ni-P comb pattern. Combs are 50 μm large and gap is between each comb is 30 μm large.
Conclusions

Electrolytic deposition of Ni-P has been studied as a potential material for MRI safe 3D electrostatic MEMS. Plating parameters of Ni-P deposits were optimized to target high phosphorus content, high deposition rate and good film adhesion. Results showed that low current densities (between $-10$ mA/cm$^2$ and $-30$ mA/cm$^2$) combined with a solution containing a low phosphorous acid concentration (5 g/l) allowed a good adherence, high phosphorus content ($>13$ wt%) and an acceptable deposition rate (0.1 $\mu$m/min). Then, structural, mechanical, electrical and magnetic properties confirmed the good properties regarding to the targeted application. Finally, 10 $\mu$m-thick Ni-P comb patterns with 13.5 wt% phosphorus content were successfully micro-molded on a 2-inch glass wafer. This result is very promising for the development of 3D MEMS based on the proposed additive process. The next step will consist in the fabrication of a 3D prototype to study fatigue, stress and MRI compatibility.

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