Novel Fabrication Process for Micro Thermoelectric Generators (µTEGs)

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Abstract. A cost effective bottom-up process for the fabrication of micro thermoelectric generators (µTEGs) was developed. It is based on a novel fabrication method involving a selectively sacrificial photoresist for the sequential galvanostatic electrodeposition of thermoelectric materials. The use of an industrial pick and placer (P&P) for dispensing the second photoresist allows for accurate and flexible µTEG designs. The process makes use of Ordyl® as a negative dry film photoresist template and sequential lamination steps for shaping all thermoelectric legs and contacts. All structures of the µTEG are generated in one photoresist multi-layer – this represents the most significant advantage of the process. The process uses a minimum of clean room processing for the preparation of pre-structured substrates for electrodeposition and therefore provides a cost-effective, highly flexible fabrication platform for research and development.

1. Introduction
Smart energy autonomous micronodes (SEAM) are one example of autonomous wireless sensor systems which have experienced increased interest during the last decade. Application areas for these systems range from medical healthcare to automotive industry. As one application, a consortium of workgroups and institutions around the University of Freiburg is - among other topics - investigating new ways of detection, analysis and treatment of diseases connected to the brain, e.g. epilepsy or Parkinson’s disease [1]. In this context implantable SEAMs have potential applications such as brainwave analysis or the autonomous neurostimulation of targeted areas within the brain. All of these applications require a reliable energy supply which shall be provided via application of a micro thermoelectric generator. Micro thermoelectric generators (µTEGs) are miniaturized TEGs and therefore able to convert thermal energy into electrical energy through the Seebeck effect. They consist of alternating n- and p-type semiconductor thermolegs placed thermally in parallel and electrically in series. The specific application of the µTEG presented in this paper is a system for transcranial energy harvesting (through the skull bone) as an energy supply for implanted SEAMs. The goal is a long lasting, maintenance-free, low energy supply without the requirement of a battery replacement.

Several different µTEG fabrication processes have been published already. The processes presented by Lim et al. [2], as well as the one by Glatz et al. [3], make use of low-cost electrodeposition to generate the required thermolegs. However, a multi-step stripping and recoating process (Ref. [2]) and the need to restructure the lower contacts at the end of the electrochemical
deposition process (Ref. [3]) must be performed in a clean room. The commercial process developed by German company Micropelt uses plasma sputtering to form the thermolegs, which is carried out in a clean room environment as well [4]. Other µTEG build-up processes involve e.g. special photosensitive glass molds for aerosol deposition [5], or magnetron sputtering [6]. There are few examples of specific low-cost µTEGs; Madan et al. used a precision dispenser to print thermoelectric components of generators [7] and Shin et al. recently published a fabrication process via electrodeposition [8].

The aim of the fabrication process described here was to reduce manufacturing complexity compared to existing processes, enabling the production of cheaper µTEGs with a minimal dependence on cleanroom technology while maintaining the ability to use very small structures in the future. The process therefore makes use of a cost effective galvanostatic electrodeposition technique developed in our labs [9–11] to generate n- and p-type thermolegs directly in pre-structured molds. The use of an industrial pick and placer (P&P) equipped with a dispensing unit allows selective sealing of pre-structured molds with photoresist and enables sequential deposition of n- and p-type thermolegs. The µTEG structures are pre-fabricated in a clean room using Ordyl® as a negative dry film photoresist. After this initial step no further clean room processing is required.

2. Fabrication Process

The fabrication process was developed for a µTEG consisting of seven thermocouples (TCs) and has been presented at the International Conference on Thermoelectrics ICT 2015, in Dresden (Germany) [12]. This process has been adapted and improved for a µTEG consisting of 71 TCs. The fabrication process for a 7 TC µTEG is shown in figure 1 and is described here for completeness. Steps a to f were carried out in a clean room environment on wafer level. The subsequent steps (g to m) were performed on diced individual chips of 15.8 x 24.8 mm size (leg ø 300 µm). High resolution printed transparency masks (Koenen GmbH, Ottobrunn, Germany) were used for UV photolithography. Alumina wafers (525 µm thick, diameter 100 mm) were used as a substrate. A 100 nm Au seed layer was thermally evaporated on top of a 10 nm Ti adhesion layer (figure 1a). A positive photoresist (AZ® 1518, MicroChemicals, Ulm, Germany) was used as a mask for wet chemical etching (aqueous KI solution followed by 1 % HF) to structure the seed layer and interconnected bottom contacts (figure 1b) that are used as plating electrodes and internal connections for the µTEG. A 17 µm thick Ordyl® laminate dry film photoresist with high chemical and thermal stability (Ordyl® SY-355, Elga Europe, Italy) was laminated on top of the substrate and structured using a maskaligner (MA6, Karl SUSS, Garching, Germany) to form a template (figure 1c) for Au electroplating of the lower contact pads (figure 1d, carried out outside the clean room). Subsequently, a second 55 µm thick Ordyl® layer was laminated on top to form a template for the µTEG thermolegs (figure 1e). This was followed by lamination of a third, 17 µm thick Ordyl® layer, structured to form a template for the upper contact structures (figure 1f). Both Ordyl® layers were developed simultaneously and hard baked at 150 °C to guarantee a high chemical stability. To allow a sequential galvanostatic electrodeposition of n- and p-type legs a P&P (SAM42, Amadyne, Bühl, Germany) with a mounted dispenser was used to apply positive photoresist drops (AZ® 1518, MicroChemicals, Ulm, Germany) locally as seeding for alternating cavities (figure 1g). The second photoresist was exposed to UV light 3 times for 10 s with 30 s intervals in between, and was subsequently hard baked at 60 °C for 20 min. All open cavities were filled with n-type Bi₂Te₃ using the pulsed electroplating process (200 ms pulse length; 10 % duty cycle; mean current density 3.3 mA/cm²) described in reference [9]. The deposition was carried out in acidic Bi/Te electrolytes as described in [9-11]. The second photoresist was selectively stripped with isopropanol (figure 1h) before sealing the previously deposited Bi₂Te₃ thermolegs the same way with the P&P as done with the other cavities (figure 1i). The deposition of the p-type material (Cu) into the new open molds was carried out the same way as described in [9]. The second set photoresist mask drops was removed by immersing the µTEG in isopropanol (figure 1i). A thin Au layer was sputtered on the sample surface and polished to ensure metal coverage inside the molds for the upper contacts.
only (figure 1l). Galvanostatic electrodeposition of Cu was used once more to generate the upper contacts (figure 1m). The Ordyl® template was preserved and acted as structural support for the TEG.

![Figure 1](image)

**Figure 1.** Steps of the multi-lamination process shown for a μTEG with 7 TCs (all heights are increased 10x for better visibility) – description is given in the text.

3. **Results and Discussion**

The complete process is discussed elsewhere [12]; in this paper only modifications to the original process are discussed. Compared to the previously published process the generator design was modified to have 71 TCs (figure 2) instead of 7, aiming for higher output voltage. Additionally, two larger single couples (not visible) were added to the deposition template which can be used for characterization purposes. For depositions of the μTEG structures only, the large couples are covered by adhesive tape, preventing any deposition during structure plating. The fabrication of the new 71-TCs generator is shown in figure 2. The key step, the sequential electrodeposition of \( n \)- and \( p \)-type thermoelectric material, is depicted in figure 2b-e, showing the photoresist pattern produced by the P&P. Modifications to the process included the change of the second photoresist from the negative resist AZ® nXT125 (MicroChemicals, Ulm, Germany) to a positive resist. The original negative photoresist has a high chemical stability and was therefore a good choice for electrolyte treatment. Due to the high stability, however, it could only be removed using acetone, which also attacked the Ordyl®-template over time possibly resulting in destroying the electroplating template. The new positive photoresist (AZ® 1518, MicroChemicals, Ulm, Germany) is less viscous and therefore easier to apply but, most important, can easily be removed by isopropanol alone. After deposition, the photoresist is exposed to UV light 3 times for 10 s with 30 s intervals in between. This step destabilizes the photoresist and makes it easily dissolvable in the solvents. The subsequent hard bake results in an increased stability towards the electrolytes, which is sufficient for deposition times up to 24 h. The subsequent removal of the sealant does not involve long treatment in acetone, but rather short exposure to isopropanol. This prevents damage to the Ordyl®-template. Copper was chosen as \( p \)-type material because of the easy deposition process. Due to the very weak thermoelectric properties of Cu, the TCs in this μTEG are actually uni-legs with the Bi₂Te₃ accounting for the thermoelectric properties and the Cu just creating the electrical connection. In future iterations of the μTEG, Cu will be replaced by other materials such as pure Te or (Bi,Sb)₂Te₃. These deposition process are currently still under investigation. As shown in figure 2a the bottom contacts are fully interconnected to provide
a uniform electrode for the electrodeposition process. For the finalized µTEG (figure 2g), these interconnects, together with the Ordyl*-template in those areas, were removed via laser ablation to electrically separate the individual TCs.

![Fabrication process as a microscope photo sequence](image)

**Figure 2.** Fabrication process as a microscope photo sequence: a) pre-structured template prepared for electrodeposition with Au contact pads and interconnects; b) half of the molds were covered by the second photoresist and n-type Bi₂Te₃ was deposited into the open molds; c) the other molds were opened with isopropanol; d) the deposited Bi₂Te₃ thermolegs were covered with a photosist layer and Cu was deposited into p-type cavities; e) both thermoleg-types were opened; the Ordyl® layer is still in place; f) after Au sputtering, and surface polishing, the upper contact molds are filled with a Au seed layer; g) electrodeposition of the Cu upper contacts; h) the Au interconnects as well as the Ordyl® layers on top are removed by a laser.

Some measurements on the new µTEG have been performed but far more will be carried out in the near future. All measurements in table 1 were carried out prior to the upper contact deposition on as-deposited samples. The electrical resistance of µTEG 1 and 3 shows low values with deviations comparable to the previous 7-TC µTEGs from reference [12]. The other two µTEGs appear to have a contact problem because measurements on different thermolegs yielded a variety of values. An improvement of the electrical properties is expected after a temperature treatment at 200 °C for several hours. The Seebeck voltage values are even higher compared to those for the previous µTEG [12].

**Table 1.** Measurement of Seebeck voltage and electrical resistance on 4 individual µTEGs; averaged values from 3 independent measurements.

| Measurement of 3… | µTEG 1 … Bi₂Te₃/Cu TCs | µTEG 2 … Bi₂Te₃ legs only | µTEG 3 … Bi₂Te₃ legs only | µTEG 4 … Bi₂Te₃ legs only |
|-------------------|-------------------------|---------------------------|---------------------------|---------------------------|
| Seebeck voltage in μV/K with sD | 57,7±1,52 | 57,0±2,10 | 51,6±0,56 | 53,2±0,52 |
| R electric in Ω with sD | 0,244±0,134 | 8,418±13,943 | 0,003±0,0003 | 32,539±37,505 |
4. Conclusion and Outlook

In the present work, a low cost approach to the fabrication of µTEGs was shown. The process exhibits two key features: the use of a multi lamination technique based on Ordyl® dry film photoresist as a chemically stable template, and the use of a P&P with a second, positive photoresist to cover individual pre-structured cavities and allow sequential electrodeposition of two different thermoelectric materials. The high flexibility of the process provides a perfect platform for research and development on thermoelectric materials as well as µTEGs as systems themselves. Initial measurements of the Seebeck voltage and the electrical resistance show promising values. In upcoming work the characterization of the µTEG will be finished and accompanied by simulations.

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