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Bio-inspired 3D funnel structures made by grayscale electron-beam patterning and selective topography equilibration



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ABSTRACT

Electron beam grayscale lithography and selective thermal polymer reflow were combined to realize replication master having a bio-inspired surface topography. It consists of an array of asymmetric denticles with two-directional gradients on different length-scales. Each denticle has a sharp pin of 2 μ m height on one and a smooth taper on the other side. In contrast to funnel-like structures having only vertical sidewalls, master with a sidewall angle smoothly changing between 15° and 70° were prepared. Discrete patterns, predefined by electron beam lithography, were transformed by reflow into well-defined, continuous, final device structures. Starting from stepped structures with only a few levels, this new approach of tapering allowed a very smooth transition from steep, sub-500 nm regions with aspect ratios up to four towards very broad and shallow regions within the same structure. This enabled the origination of master structures to be used for replication as low-frictional, durable, bio-inspired surfaces by ceramic powder injection molding.

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1. Introduction

Inspiration of engineers by biological models is a common approach to create functional products and surfaces. These models are mostly complex and consist of hierarchical structures spanning size ranges from micro- to nanometer [1]. Engineering functional surfaces requires a transfer of the bio-concepts into structures that can be realized by scalable and robust fabrication processes. Possible inspiration comes from snake-skins having surface features enabling low friction in a preferred moving direction [2]. For example sand-swimming reptiles, like the sandfish, have micro-structures on there skin that allow them, in combination with the biochemical composition of the structures, to move in sand with very low friction [3]. Shark denticles are also developed by nature to reduce the fluid-drag in water [4].

This paper presents an engineered surface which was inspired by low-frictional surfaces like the mentioned ones and was designed for a robust fabrication process. The basic concept of fabrication comprises a mastering by means of lithography and a subsequent replication of this master by imprint-based lithography [5] and ceramic powder injection molding. The replication process is detailed elsewhere [6]. This contribution discusses the mastering by a process termed temperature activated selective topography equilibration (TASTE) [7]. This mainly involves electron beam grayscale lithography and thermoplastic polymer reflow. The new contribution of this work is the realization of ultra-smooth heightgradients in two directions in difference to other work on tapered structures with a height-gradient only in one direction [8,9].

2. Experimental

2.1. Structural challenges

The designed surface topology comprises a periodic repetition of asymmetric denticles with a sharp pin on one and smooth tapers on the other side. The denticles measure about 3.3 μ m in width, 7.3 μ m in length as well as 2.0 μ m in height. The design was provided by E. Broell GmbH & Co. KG. A group of three denticles is shown in Fig. 1. Basically, the denticles comprise height-gradients in *x*- and *y*-direction over different length-scales. Previous work showed the successful transformation of stepped structures into smooth height-gradients using the TASTE process [10,9]. However, there gradients were only considered on one length-scale. The creep-like polymer reflow during TASTE is well understood and was recently simulated by a soap-film method [11,12]. This allows



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the prediction of final reflow structures starting for example from structures having only a few steps. The particular technical challenge of the denticle-like structure in this work is the mentioned gradients. They require high aspect ratios (above 4) and small features (below 500 nm) as well as very steep (about 70°) and very shallow (about 15°) slopes with smooth transitions within the same structure.

2.2. TASTE process

TASTE is based on the selective reflow of polymer regions with different glass transition temperatures T_g [7]. The reflow temperature is usually set to be close to the highest T_g within these polymer regions. In the variation of TASTE used in this work, the simultaneous change of the molecular weight M_w [13,7] and the T_{g} [7] due to electron beam exposure of thermoplastic resists is exploited. Doses required for certain step heights are extracted from the resist contrast curve. The discrete, lateral exposure dose variation (Fig. 2a) results in a respective lateral M_w -variation. The larger the exposure dose, the smaller is the resulting M_w and the larger is the respective wet-development rate. Thus, discrete height-steps in the resist can be achieved (Fig. 2b). Using this, two process variants are possible to realize the denticles shown above either as convex or concave structures (cf. Fig. 2). Both, completely cleared regions without any resist or regions having a thin residual resist layer are feasible. Larger exposure doses give smaller T_g -values [7] and a faster reflow at a given temperature [11]. By adjusting the reflow temperature and reflow time, different geometries are accessible (Fig. 2c). Due to the creep-like reflow behavior close to Tg, quasi-pinning on non-exposed, stabilizing areas and along the cleared substrate regions could occur as intermediate reflow state. With reflow temperatures above the glass transition, previously stable structures can also be reflowed to give a more rounded profile. With very long reflow times or high reflow temperatures, the guasi-pinning on the substrate can also be overcome. Furthermore, thin residual layers act as wetting film. All of this can be used to achieve more rounded structures at the bottom of concave profile sections.

In terms of replication, the two process variants can be considered as positive (convex) or negative (concave) tone structures (Figs. 2 and 3). The advantage of the positive process is its direct usability for mold-casting. The master structure already has the correct tone as required in the final product. The main advantage



Fig. 1. 3D-CAD design of three denticles of the desired bio-inspired structure. Finally, these structures with (1) high aspect ratios and (2) very steep and very shallow slopes with smooth transitions at the same time are required to be replicated in a ceramic material.

of the negative process is the higher stability of the structure due to large stabilizing areas surrounding the exposed areas. An additional advantage in this work was the reduced electron beam writing time for negative structures due to the lower area coverage of beam-exposed structures. Multiple tone inversion steps can be used later during replication to achieve the correct final tone. This gives the freedom to decide for the most appropriate master origination process.

2.3. Grayscale exposure and reflow

The used poly (methyl methacrylate) (PMMA) resist was mrI-PMMA120k (micro resist technology GmbH). The resist was spincoated on blank silicon wafers to give an about 1950 nm thick initial film and soft-baked for 2 min at 140 °C. The electron beam grayscale exposure was done with a 100 kV system (VISTEC EBPG 5000 Plus) using doses up to 455 μ C/cm² (dose-to-clear). This resulted in a reduction of the initial M_w from 91.2 kg/mol to below 8.9 kg/mol as well as of the T_g from about 120 °C to below 90 °C [7]. After exposure, the samples were developed for 60 s in 4methylpentan-2-one (MIBK) at 20 °C, rinsed with 2-propanol and deionized water and blown dry with nitrogen. Finally, the samples were placed on a hotplate for a global reflow at a fixed time and temperature. After reflow, the samples were immediately cooled to room temperature to freeze the reflow structures.

2.4. Process design

The desired final structure is sketched as height distribution in Fig. 3a and as a width-cross section in Fig. 3b. For the positive process, elevated steps with cleared surroundings are produced the PMMA resist (Fig. 3c, hatched). After reflow, this gives a structure as depicted in Fig. 3c (dashed line). For negative structures, a recessed-step structure is realized in the PMMA resist (Fig. 3d, hatched). After reflow, a recessed and continuous profile as



Fig. 2. Convex and concave profiles realized by (a) electron beam lithography with a discrete dose profile, (b) subsequent, dose-dependent removal of exposed resist and (c) final, global thermoplastic reflow.

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