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Fabrication of Micro Structured Dental Implant Abutments for Optimized Soft Tissue Integration

Abstract: Within this work we demonstrate a UV-Lithography based method for the fabrication of microgrooves on titanium surfaces. The microgroove period, depth and profile form are easily controllable by process parameters. By controlled under-etching of a lithographically structured photo resist, different profile forms from nearly rectangular, over curvy/spiked to sinus-shaped forms with different amplitudes and sizes can be realized. The resulting microgrooves can be directly used as implant or implant abutment surfaces to enhance soft tissue integration or to create molds for cell/substrate interaction studies. Due to the lithographic process the whole method is highly controllable and reproducible.

Keywords: Soft-Tissue Integration, Dental Implant Abutments, Microgrooves, Ti6Al4V.

https://doi.org/10.1515/cdbme-2018-0163

1 Introduction

The success of an implantation of a dental implant is often reduced by a lack of attachment of the surrounding soft tissue [1]. If there is a faulty or just a partial connection between the surrounding soft tissue and the implant abutment surface, bacteria can get to the underlying bone and can cause inflammation or even chronic infections [1]. The result of such infections is often a complete loss of the implant.

It is known that the attachment of gingival fibroblast cells can be optimized by applying a microstructure in form of microgrooves to the implant abutment surface [2, 3]. Such structures can have a positive effect on the soft tissue integration [4]. The manufacturing of such structures is often realized by laser ablation [5-7]. However this manufacturing method can have some disadvantages with local heat affected zones altering the material or residue of melted material. As a different approach for structuring commercial pure Titanium (cpTi) and the alloy Titanium gr. Ti6Al4V to create microgrooves we have tested the ability of a lithographic based manufacturing process in combination with wet-etching. A similar process was already described in [2] and has shown positive effects on soft tissue integration but the exact surface topography was not clearly defined and no different microgroove geometries were created.

2 Materials and Methods

2.1 Substrate Material

Commercially pure Titanium Grade 4 (cpTi) and the alloy Titanium Grade 5 ELI (Ti6Al4V) material was provided by Cendres+Métaux SA, (Biel, Switzerland) as 1 meter long rods with diameters of 8 mm.

2.2 Sample Preparation

To be able to inspect unique points on each sample a 2 mm wide flat was milled into the bars, which was used as a reference within manual or automated measurement equipment like microscopes, Atomic Force Microscopy or Scanning Electron Microscopy. The bars were cut into 2 mm thick disks by electro discharge wire erosion. To remove the heat afflicted zone and residue of carbon and other impurities due to the wire erosion process the samples were placed on a flange and grinded and polished. For each batch of production 91 samples were successively grinded with silicon

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carbide paper of different grit sizes (P400-P2500, Struers GmbH). Between each grinding step the sample holder was intensely cleaned by rinsing with deionized (DI) water to remove residues of the previous step. To recognize individual samples, the backside of each sample was uniquely marked with batch and sample number by a Laser marking system. The samples were removed from the flange, cleaned in an ultrasonic bath for 10 minutes in 2-propanol followed by DI-water for 10 minutes and dried by compressed nitrogen. The samples were turned and the front side was also grinded in the same procedure as the backside. To achieve an adequate flat surface for UV-lithography the samples were then mechanically/chemically polished. Both the cpTi and the Ti6Al4V samples were polished with a mixture (9:1) of a colloidal silicon particle solution (OP-S Nondry, Struers GmbH) and Hydrogen Peroxide (31%, BASF SE) for 30 min at 150 rpm and a force of 20 N (polishing machine Saphir 355, ATM GmbH). After polishing, the samples were removed from the flange and cleaned successively in ultrasonic baths of acetone, 2-propanol, and DI-water for 10 min each and then dried by compressed nitrogen.

2.3 Initial Sample Characterization

17 Samples per batch were taken for initial surface characterisation. The characterization included surface roughness and contact angle measurements. The average roughness values (R_a) for the Ti6AL4V samples were smaller than 1 nm and for the cpTi smaller 3 nm (**Table. 1**). Measurements were taken using a Vertical Scanning Interferometer (VSI, ContourGT, Bruker Corp.) using Phase Shift Imaging Mode with a field of interest of 170 x 130 µm². Three individual measurements per sample were taken. A plane-tilt error correction was applied. Contact angle measurements were also carried out at three spots on each sample resulting in an average value per sample. Measurements were performed with a contact angle measurement system (40 Micro, DataPhysics GmbH) and droplet volume was set to 4 µl. Measurement procedure was kept strictly similar in timing to get reproducible result. The average value for the cpTi is 70° while the average value for the Ti6Al4V is 75°. Both surfaces are hydrophilic.

Table 1: Average Roughness (R_a and R_t) values of the grinded and polished cpTi and Ti6Al4V samples.

Material	R_a [nm]	R_t [nm]
cpTi	2.0 +- 0.8	72.6 +- 14.6
Ti6Al4V	0.7 +- 0.1	10.6 +- 3.2

2.4 UV-Lithography

For UV-Lithography the samples have to be coated with a negative or positive tone photoresist. Depending on the tone of the resists used the exposed or the unexposed area can be removed by development. In case of silicon based substrates a conditioning step would normally be used to make sure that the photoresist adheres to the substrate. Since Titanium is likely to oxidize within Oxygen plasma and primers are optimized for silicon substrates, this step was not performed. To make sure that there are no adhesion issues, a cleaning procedure of acetone rinsing followed by 2-propanol rinsing followed by rinsing with DI-water was performed before each coating. After rinsing the samples were dried by compressed nitrogen. To minimize adhesion problems due to a possible remaining water layer a dehydration bake was performed at 150°C for at least 5 minutes. After cooling down the coating procedure immediately started. As resist a positive tone photo resist (AZ4533, Merck Performance Materials GmbH) was used. The parameters for spin coating were 4000 rpm for a period of 60 s, with an acceleration ramp of 1500 rpm/s. After coating a so called softbake on a hotplate was carried out at 95°C for 5 min to evaporate the remaining solvent. This procedure resulted in an average resist thickness of 4 µm (measured by vertical scanning interferometer after dose variation and fabrication of test samples). The complete UV-lithographic process is shown in **Figure 1**.

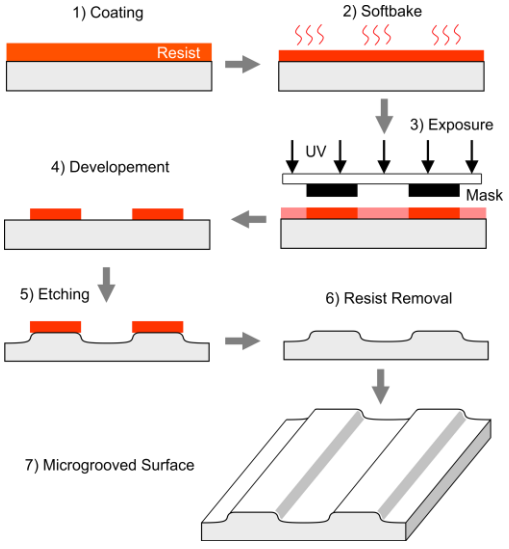

Figure 1: Schematic drawing of the UV-lithography process: (1) Coating, (2) Softbake, (3) Exposure by UV-light using a chromium-glass mask. (4) Development of the exposed areas, (5) Etching will copy the developed resist pattern into the material, (6) Resist removal (7) Resulting Microgrooved Surface.

For structuring the coated samples were then exposed to UV-light at a wavelength of 405 nm using a flood exposure system (LH5, Suss MicroTec AG). To achieve different structures, chromium line masks with periods ranging from 3 µm to 200 µm and ridge to groove ratios reaching from 1:1 to 1:3.3 were used. After exposure of the samples with a dose of 120 J/cm^2 the samples were developed in a mixture of AZ400K developer solution (Merck Performance Materials GmbH) and DI-water (1:4) for 2 min. The samples were rinsed with DI-water and blown dry by compressed N_2.

2.5 Wet Etching

To transfer the developed resist pattern into the Titanium substrates and to form different microgroove profiles, samples were wet etched for various times reaching from a few seconds to several minutes depending on the line mask sizes and the desired profile form. As etchant a mixture of Hydrogen Fluoride (5%, BASF SE) and Hydrogen Peroxide (31%, BASF SE) and DI-Water (11 HF: 1 H_2O_2: 10 H_2O) was used. The etch rate for cpTi was determined to be 3.9 µm per min and the rate for the Ti6Al4V was determined to be 2.4 µm per min. After the etching procedure the samples were cleaned in a DI-water bath and dried with compressed nitrogen. The remaining resist was stripped off using pure AZ400K developer. After stripping a second etch step was performed for a subset of samples to remove the polished surface and to get a homogenous surface structure. The etching was performed using the same etchant and conditions but a reduced etch time of just 5 s, thus removing only 150 to 300 nm of the top layer.

2.6 Post Process Characterization

All samples have been characterized by Scanning Electron Microscopy (Supra VP 60, Carl Zeiss AG) using an Extra High Tension of 5 kV and different magnifications between 100× and 10,000×. Some samples have been tilted to 30°, 45° and nearly 90°-angle to show the three-dimensional structures. To get information about the exact three-dimensional profile forms all samples have been characterized using a Vertical Scanning Interferometer at a magnification of 50× and 500×. Height and length measurements have been carried out manually with the machine's built-in measurement software. For analysis a tilt-correction filter was applied. For visualization purposes only an additional interpolation filter was applied. Exemplary results are shown in **Figure 2**.

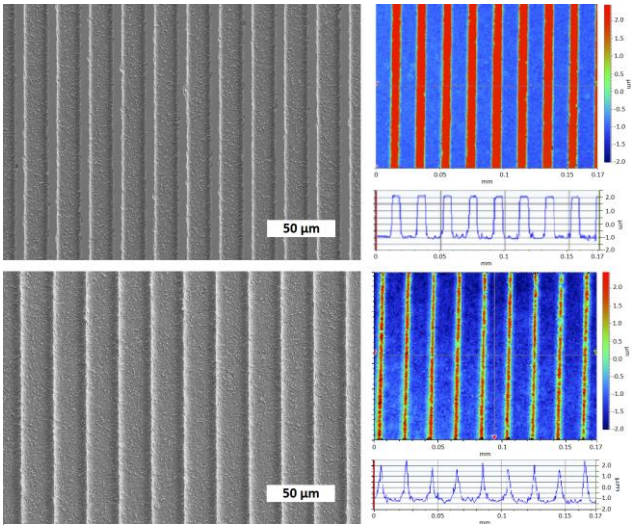

Figure 2: Exemplary results of characterization using Scanning Electron Microscopy and Vertical Scanning Interferometry for two different etching times (top: 30 s; bottom: 120 s). The scanning electron micrographs on the left show Ti6Al4V samples lithographically structured with a 20 µm period mask with 1:1 ridge/groove ratio and the corresponding VSI measurements on the right.

3 Results

Depending on process parameters like line mask width and etching time a broad variety of different profile forms can be realized. The Scanning Electron Micrographs in Figure 2 show the results for a 10 µm line mask with 1:1 ridge to groove ratio for etching times of 30 s and 120 s. With longer etching times the resist pattern gets completely under-etched resulting in a concave surface profile with a period twice the line mask width. Figure 2 also shows the corresponding VSI measurements of the same samples with their 3D profiles. Since the etching process is isotropic, the grooves are getting linearly bigger and deeper until the patterned resist is fully under-etched and a concave profile with sharp spikes results. Further etching results in a softening of those structures resulting in sinus-shaped forms. By variation of etching parameters and setup, many different surface profiles were realized. In **Figure 3** a schematic overview of the influences and possible surface profiles is shown. The variation of time for a fixed ridge/groove ratio will result in a change of the form of the microgrooves (nearly rectangular over curvy/spiked to sinus-shaped). The changes of the line mask width and the ridge/groove ratio will change the period and the proportion of grooves to ridges. By variation of all three parameters a broad variety of profile forms for sizes in the range of 1.5 to 100 µm are realizable.

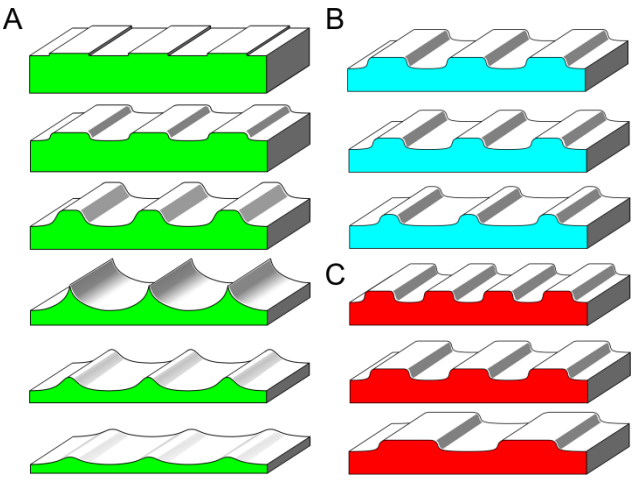

Figure 3: Schematic drawing of possible profile forms and influencing parameters: (A) Etch time increasing from top to bottom. (B) Variation of ridge/groove ratio. (C) Variation of line mask size. The structured photo resist layers are not shown.

4 Conclusion

UV-lithography combined with wet etching is an easy and highly reproducible method to manufacture microgrooved surfaces. By controlled under-etching of a patterned photo resist it is possible to not only produce nearly square shaped profiles but also spiky/curvy to complete sinus-shaped profile forms are realizable. The UV-lithographic process on cpTi and Ti6Al4V disks with diameters of 8 mm can be handled like wafer based processes. Essential for the process is a flat and smooth surface which can be made by grinding and mechanically/chemically polishing using a mixture of a colloidal silicon particle solution and hydrogen peroxide. The grinding and polishing method ends in extreme flat and smooth surfaces with average roughness values of smaller than 1 nm for Ti6Al4V and smaller than 3 nm for cpTi respectively. To realize different lateral groove sizes, chromium/glass masks with different line widths and ridge to groove ratios can be used. The presented method is a well controllable and reproducible manufacturing method for creating microgrooves of various shapes and sizes on cpTi and Ti6Al4V. Due to the underlying lithographic process the lateral precision of the structures only depends on the mask alignment and the quality of the lithographic depiction. The vertical precision and form tolerance of the microgrooves is limited to the material composition, the crystal structure and the etching process. The resulting microgrooved surfaces can be used as dental implant or implant abutment surfaces to enhance soft-tissue integration or alternatively as molds for imprint lithography to create substrates for cell/surface interaction studies. Additionally a nanostructure can be applied to achieve a micro- and nanostructured surface [8]. The transfer to 3D shapes can be realized by Rotational Lithography.

Acknowledgment

Authors would like to thank Cendres+Métaux SA for providing the titanium material and U. Köhler and H Fornasier for their help with hydrofluoric etching.

Author Statement

This Work has been funded by the German Federal Ministry for Economic Affairs and Energy (BMWi) within the Innovation Programme ZIM for small and middle size companies (No. KF2308206KJ4). Authors state no conflict of interest.

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