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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 distance, depth and profile form are easily controllable by process parameters. By controlled under etching of a lithographic mask, 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: Microgrooves, Soft-Tissue Integration, Dental Implant Abutments, Ti6Al4V.

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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 more 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] and also that such structures can have a positive effects on the soft tissue integration [4]. The manufacturing of such structures is often realized by laser ablation [5-7]. However this manufacturing method might 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 and 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 it showed 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 Abutment Material

Commercially pure titanium grade 4 (cpTi) and the alloy titanium grade 5 ELI (Ti6Al4V) material was provided by Cendres+Métaux SA, (Biel, Switzerland). The material was provided 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 grinded with silicon carbide paper (P400-P2500, Struers, Germany). Between each

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grinding step the complete sample holder was intensely cleaned by rinsing with DI-water to remove residues of the previous step. To recognize individual samples one side of each sample was uniquely marked containing 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 backside was also grinded in the same procedure as the other side. To achieve an adequate flat surface finish 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) and Hydrogen Peroxide (31%, Merck) for 30 minutes at 150 rpm and a pressure of 20 N.

2.3 Initial Sample Characterisation

17 Samples per batch were taken for initial surface characterisation. The initial characterization included surface roughness and contact angle measurements. The average roughness values (Ra) for the Ti6AL4V samples were smaller than 1 nm and for the cpTi smaller 5 nm (**Table. 1**). Measurements were taken using a Vertical Scanning Interferometer (VSI, Bruker ContourGT) using Phase Shift imaging Mode with a field of interest of 170 x 130 μm^2. Three individual Measurements at three points 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 contact angle measurement system (Data Physics 40 Micro) and drop size was set to 4 µl. Measurement procedure was kept strictly similar in timing to get reproducible measurements. The average values for the cpTi is 70° while the average value for the Ti6Al4V is 75°. Both surfaces show the typical hydrophilic behaviour.

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 are-as will 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 oxidise 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 the samples were prebaked 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) was used. The parameters for spin coating were 4000 rpm, acceleration ramp of 1500 rpm/s for a period of 60 s. After coating a so called soft bake on a hotplate at 95°C for 5 min was carried out 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**.

Table 1: Average Roughness values of the grinded and polished cpTi and Ti6Al4V samples.

Material	**R_a**	**R_t**
cpTi	2.0 +- 0.8	72.6 +- 14.6
Ti6Al4V	0.7 +- 0.1	10.6 +- 3.2

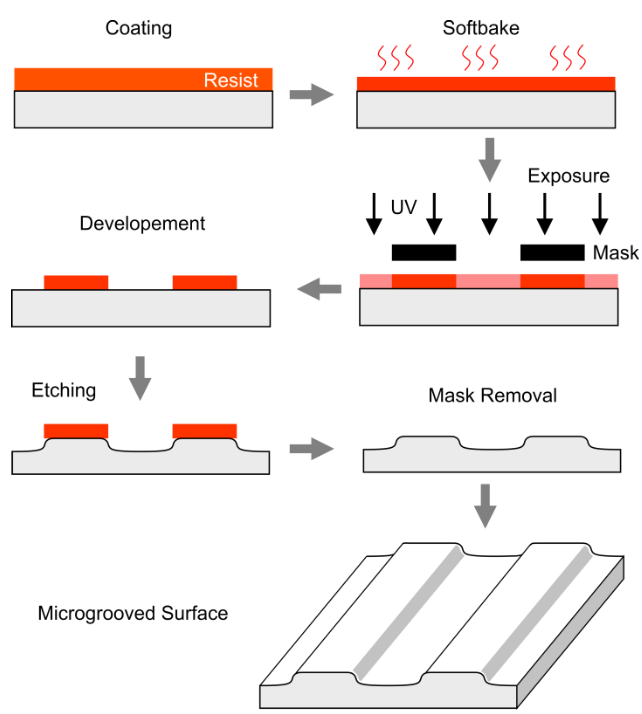

Figure 1: Schematic drawing of the UV-lithography (1) coating, (2) softbake, (3) exposure by UV-light using a chromium-glass mask. (4) development removes the exposed areas, (5) etching will copy the mask into the material, (6) resist removal (7) resulting microgrooved surface.

For structuring the coated samples were then exposed to UV-Light at a wavelength of 405 nm using a flood expo-sure system (Suss MicroTec LH5). To achieve different structures chromium line masks with periods ranging from 1.5 µm to 100 µm and duty cycles reaching from 1:1 to 1:1.5 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) 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 copy the masks 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, Germany) and Hydrogen Peroxide (31%) (BASF, Germany) and deionised Water (11 HF: 1 H_2O_2: 10 H_2O) was used. The etch rate for cpTi was determined to be 3.2 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 photomasks were stripped off using acetone. Afterwards the samples were cleaned by rinsing with 2-propanol followed by DI-water and dried by com-pressed N_2. After removing of the photo mask a second etch step was performed to remove the polished surface and to get a homogenous surface structure. The etching was performed using same etchant and conditions but just for 5 s thus removing only 150 to 250 nm of the top layer.

2.6 Post Process Characterisation

All samples have been characterized by Scanning Electron Microscopy using an Extra High Tension of 5 kV and different magnifications between 100 x and 10000 x. 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 Interferometry at 50 x and 500 x magnification. Height and length measurements have been carried out manually with the machines build in measurement software. For analysis only a tilt-correction filter was applied. For visualization purposes only an additional interpolation filter was applied. Exemplary results are shown in **Figure 2**.

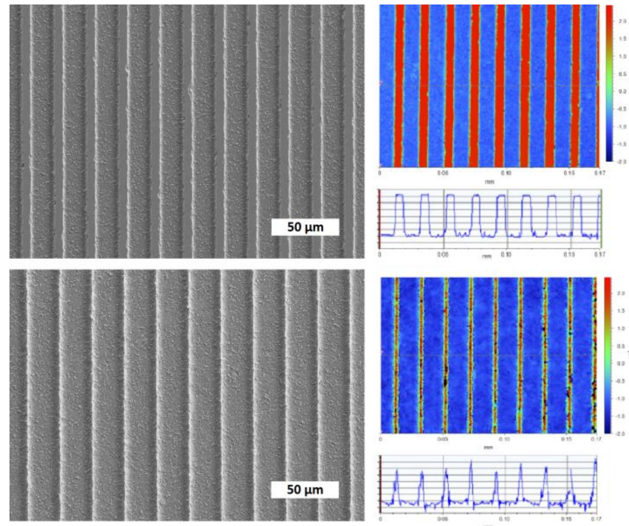

Figure 2: Exemplary results of characterization using Scanning Electron Microscopy and vertical scanning interferometry. The Scanning Electron Micrographs on the left show Ti6Al4V samples lithographically structured with a 10 µm period mask with 50/50 bridge/groove ratio and the corresponding VSI measurements on the right. Etching times top: 30 s, bottom: 45 s. Scale bars: 50 um.

3 Results

Depending on process parameters like 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 50/50 duty cycle for 30 s and 120 s. With longer etching times the mask 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. In case of an isotropic etching process the grooves are getting linearly bigger and deeper until the mask is fully under etched and a concave profile with sharp spikes results. If the etch process is kept for longer duration the curved/spiky structures will become sinus-shaped. 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 are shown. The variation of time for a bridge/groove ratio will result in a change of the form of the microgrooves (nearly rectangular over curvy/spiked to sine-like). The changes of the line mask width and the bridge/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.

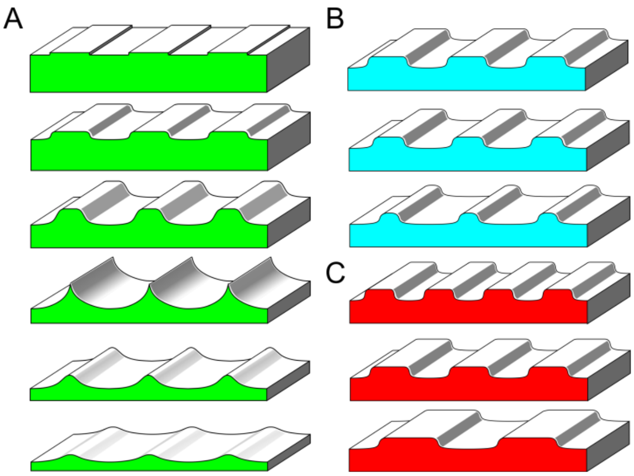

Figure 3: Schematic drawing of possible profile forms and influencing parameters time (A) Time increasing from top to bottom. (B) Variation of bridge/groove ratio. (C) Variation of line mask size (C). Masks are not shown.

4 Conclusion

UV-lithography combined with wet etching is an easy and highly reproducible method to manufacture micro-grooved surfaces. By controlled under etching of the resist it is possible to not only produce square shaped profiles but also spiky/curvy to complete sinus-shaped like 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 Hydrogen Fluoride and Hydrogen Peroxide. This 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 3nm for cpTi respectively. To realize different lateral groove sizes, chromium/glass masks with different line widths and bridge to gap ratios can be used. The presented method is a well controllable and reproducible manufacturing method for creating micro-grooves of various shapes and sizes on cpTi and Ti6Al4V. These microgrooved surfaces can be used as dental implant or implant abutment surfaces to enhance soft-tissue integration or as molds for imprint lithography to create substrates for cell/surface interaction studies.

Author Statement

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