Titanium Electrochemical Micromachining using Laser Lithography on Oxide Film

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Introduction

Due to its good mechanical properties and chemical inertness, titanium is a material of choice for implantable devices in medicine and dentistry. For many such applications the surface topography must be carefully controlled to achieve optimum cell adhesion and differentiation[1]. Electrochemical micromachining is a useful method for the fabrication of well defined surface structures in the micrometer range[2]. Normally, in electrochemical micromachining anodic dissolution is carried out through a suitably patterned photoresist, but this technique is limited to planar surfaces. Recently, it has been found that in electrochemical micromachining of titanium a patterned anodic oxide film can assume the function of the photoresist[3]. The feasibility of using direct laser writing on anodized titanium for creating patterns for electrochemical micromachining has been demonstrated[4]. Our aim is now to understand the physical phenomenon taking place during laser irradiation.

Experimental

The different steps of the novel electrochemical process are shown on the left of Fig. 1, illustrating results are presented on the right side of the figure. The experimental details of individual steps are described thereafter.

Formation of passive films

Passive films were formed on titanium surfaces in a 0.5 M sulfuric acid solution. Mirror polished titanium disks were anodized by applying a 20 V s^{-1} ramp until the anode potential reached 100 V.

Local laser irradiation of oxide film

The samples were locally irradiated using a long pulse XeCl eximer laser. A simple convergent lens was used to project the image of a mask on the surface. For the illustrating results presented thereafter, lines were written by moving the sample in front of the beam.

Electrochemical dissolution of titanium

Electrochemical dissolution of the oxide-patterned electrodes was performed in an electropolishing electrolyte containing 3 M sulfuric acid in methanol[4].

Ultra-sonic cleaning

In a last process step, the free standing oxide film resulting from underetching was removed in an ultra-sonic water bath.

Results

To gain an insight into the mechanisms responsible for the sensitizing of the irradiated zone, several analysis techniques have been used. Spectro-reflectometry measurements revealed the disappearance of the surface film after irradiation. However the depth of the crater measured by AFM showed that the oxide film was only partially removed. Surface analysis was performed to explain this discrepancy. Fig. 2 a) presents an Auger depth profile of the anodic oxide showing a steep interface between the film and the bulk titanium. Fig. 2 b) shows an Auger depth profile of the irradiated zone; it appears that a considerable amount of oxygen is still present. It could also be observed that a diffuse interface exists which is better described as a progressive transition. Recent XPS results suggest that titanium is in metallic state over the whole considered depth and hence that the oxygen of the initial oxide has diffused into the metal.

References

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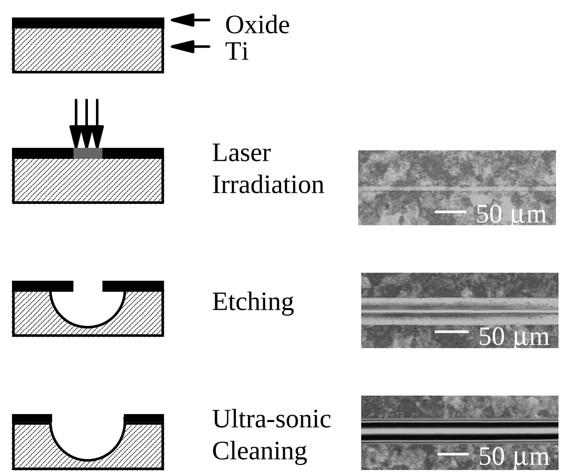

Fig. 1 Processing steps for laser electrochemical micromachining of titanium. After anodic oxidation, serial pulsed laser writing allows for flexible and rapid patterning. Selective electrochemical dissolution of the irradiated features is followed by ultra-sonic cleaning to remove the free standing oxide.

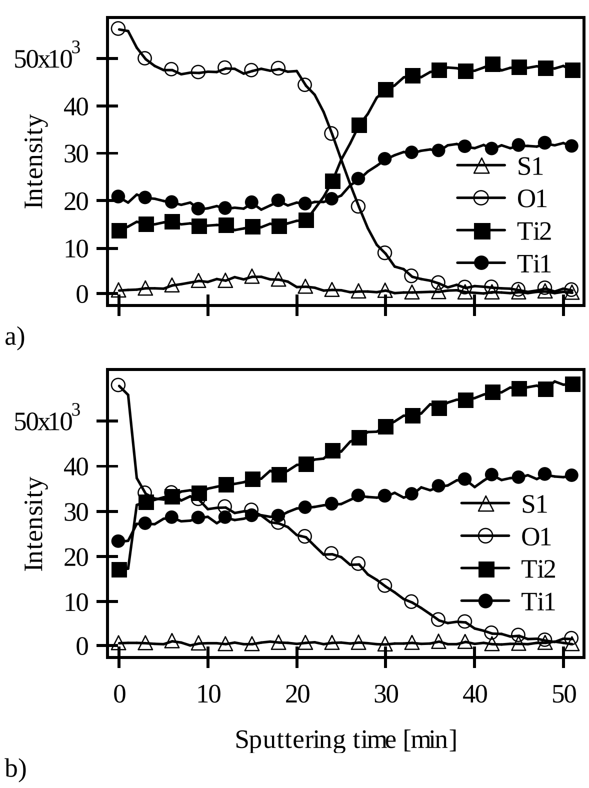

Fig. 2 Auger depth profile of (a) the anodic oxide and (b) the high fluence irradiation zone.