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Nanoporous titania films produced by pulsed interference lithography

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***Abstract*. We describe a simple, inexpensive technique for producing deep nanopores on the surface of titania films using laser exposure in a four-beam interference configuration. In addition to producing nanopores, laser pulses convert amorphous titania films to a polycrystalline state. The effect of laser exposure on the TiO_2 surface can be used to improve its biophotocatalytic properties, optimise solar cells, etc.**

Keywords: *nanoporous structures, high-power radiation interference, titania crystallisation.*

1. Introduction

The properties of titania have been the subject of intense research because this material is potentially attractive for a variety of applications, in particular for the fabrication of inexpensive, reliable solar cells [1–6]. The study of photobiocatalysis [7–11], including hydrogen generation through water decomposition in the presence of TiO_2 [12–15], is of considerable practical interest. The application field of titania has been reviewed in sufficient detail by Permenova [16]. Titania offers high chemical stability, biocompatibility, and a large index of refraction (above 2) in the IR and visible spectral regions. These properties are important for the fabrication of diffraction gratings, photonic crystals, and molecular separators. Many of the above applications require porous TiO_2 films, which can be produced by ion-beam processing. It is well known that a large surface area of catalysts enhances their effectiveness. There is considerable interest in techniques for producing nanopores in various materials, such as germanium, silicon, and SiN [17–20].

2. Experimental results

In our experiments, nanoporous TiO_2 films were produced using high-power XeCl laser pulses in a four-beam interference configuration. This approach has the advantage that nanopores result from direct laser exposure in a single-step process. As a consequence, there is no surface contamination, which may be vital for technological applications. The laser output had the following parameters: pulse energy, up to 200 mJ; pulse duration, 15–20 ns; near diffraction-limited beam divergence; coherence length above 30 cm. Dielectric mirrors were used to split the laser beam into four beams and to recombine them on the film surface. The laser configuration and four-beam interference system were described elsewhere [21–23]. Two beams were TE-polarised and the other two were TM-polarised. At the angles of incidence we used, this polarisation distribution ensured effective interference of the four beams. Nanopores were produced by two procedures: exposure of the films to one or two laser pulses. The TiO_2 films were grown by a sol-gel process on quartz substrates and ranged in thickness from 450 to 650 nm.

Figure 1 shows an atomic force microscopy (AFM) image of a TiO_2 film after exposure to a single laser pulse. In those experiments, the laser energy density delivered to

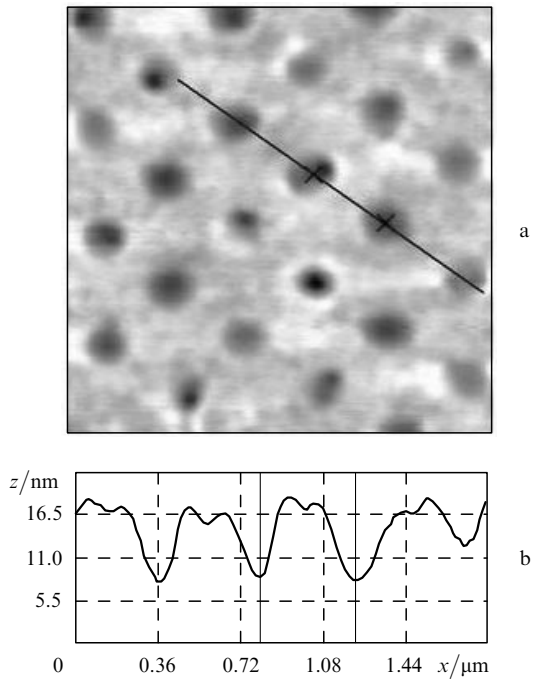

Figure 1. (a) AFM image of a TiO_2 film after exposure to a single laser pulse in a four-beam interference configuration; (b) height profile along the solid line in panel (a).

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the sample was ~ 300 mJ cm^{-2}. Our measurements showed that the pores were no more than 30 nm deep. Such pores increase the surface area only slightly.

Two laser pulses had a markedly different effect on the film surface (Fig. 2). The laser energy density was varied from 300 to 500 mJ cm^{-2}. Topography data processing showed that the surface height difference ranged from 320 to 600 nm. The large height difference on the film surface ensured an increase in surface area by more than 50%.

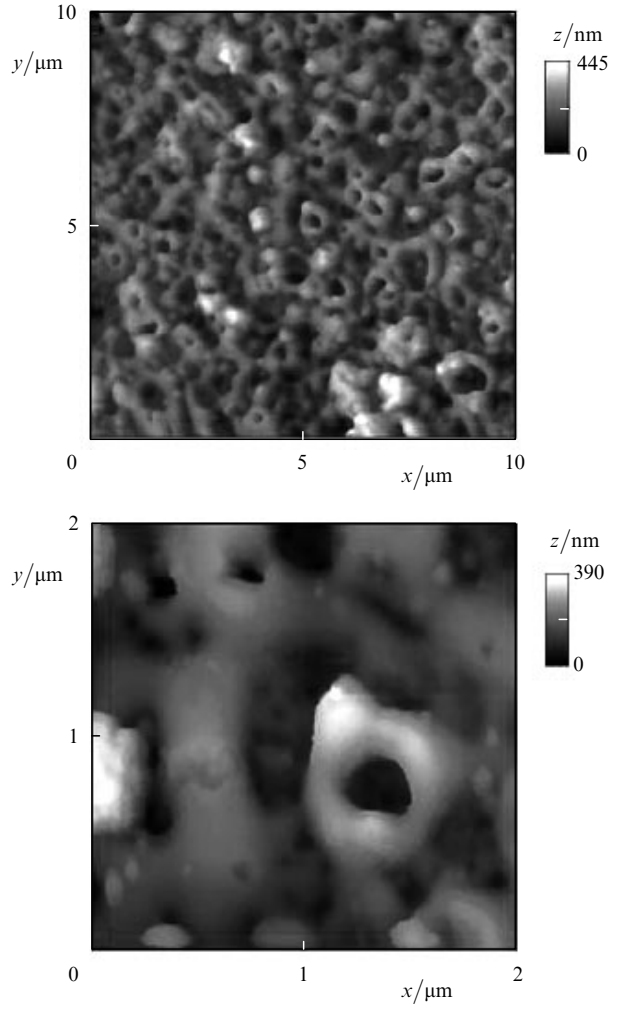

Figure 2. AFM images of a TiO_2 film (different magnifications) after exposure to two laser pulses in a four-beam interference configuration.

In our experiments, we observed a useful effect of laser exposure: film crystallisation. The as-grown films were amorphous, as illustrated by the electron diffraction pattern in Fig. 3. The measurements were made on an EMR-102 electron diffraction unit in back-reflection mode at an accelerating voltage of 50 kV. After the laser exposure, the film was polycrystalline, as evidenced by the rings in the electron diffraction pattern in Fig. 4.

The marked difference between the effects of one laser pulse and two pulses on the titania film surface can be understood in terms of the following processes: An amorphous film produced by a sol-gel process has a fine-grained microstructure and a high threshold for laser-induced effects. The first laser pulse renders the film polycrystalline

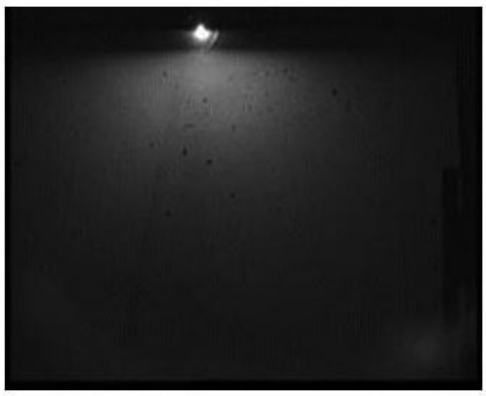

Figure 3. Electron diffraction pattern of an as-grown titania film (EMR-102 unit).

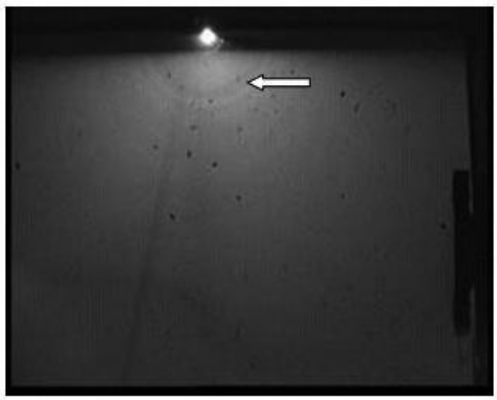

Figure 4. Electron diffraction pattern of a laser-processed titania film (EMR-102 unit). The arrow marks electron diffraction rings.

and lowers the threshold. The second laser pulse strikes the (looser) polycrystalline film, producing nanopores 350 – 650 nm in depth, which exceeds the depth of the nanopores produced by the first pulse by a factor of 10 – 20.

3. Conclusions

We have demonstrated an inexpensive method for producing deep nanopores on the surface of titania, which takes advantage of the interference of four high-power coherent laser beams. The effect of laser exposure on the TiO_2 surface can be used to improve its biophotocatalytic properties, optimise solar cells, etc. We plan to study the bactericidal properties of nanoporous TiO_2 films in the near future.

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