Femtosecond laser-induced TiO_2 nanostructures on titanium

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Abstract: We report formation of polarization-dependent nanostructures (nanolines, nanocircles) by high repetition-rate femtosecond laser pulses on titanium surface through a novel mechanism, converting Ti to TiO_2. Arbitrarily large-area patterns are created by self-stitching of these patterns.

OCIS codes: (320.7090) Ultrafast Laser; (140.3390) Laser material processing

In recent years, femtosecond laser processing has been demonstrated to be a promising technology for surface nanostructuring of metals and semiconductors [1–4]. Nanostructuring of a variety of materials is gaining widespread importance owing to ever increasing applications of nanostructures in numerous fields such as microelectronics and microelectromechanical systems, patterning for field-emitting displays. Ultra-short-pulse laser radiation has been shown to be highly effective for precision material processing and surface micro-modification because of minimal thermal and mechanical damage in various materials.

Here, we report the formation of regular nanoscale grating-like structures (nanolines) on Ti surfaces with polarized femtosecond laser radiation under regular atmosphere. These self-organized nanostructures, which appear as protrusions on the Ti surface, are made of TiO_2 (of rutile form, as determined from Raman spectroscopy). The structures appear only if the peak laser intensity exceeds a sharp threshold level.

A schematic of the experimental set-up is shown in Fig. 1. The laser source is a homemade, all-fiber-integrated Yb amplifier seeded by a wave-breaking free Yb fiber oscillator. The laser delivers 150-200 fs pulses with up to 1 μJ pulse energy, at 1 MHz repetition rate, centered at 1040 nm. The beam is focused onto a highly polished Ti surface sample with a spot size of ~11 μm (half-width for $1/e^2$ intensity). The sample is placed on a 3D motorized stage. Fig. 2(a) shows the SEM of nanolines formed by scanning the beam at a rate of 3 μm/s for an average incident power of 95 mW (95 nJ pulse energy). The scan rate corresponds to >1 million pulses being incident on any given spot, *i.e.*, one can safely regard these structures as adiabatically formed. Any beam interference effect can be safely ruled out, since it would be washed over as the beam very slowly scans over the surface.

The height of each nanoline is about 200 nm as indicated by the AFM view (Fig. 1(b)). The cross-sections of the nanolines appear to be parabolic, which suggests explosive growth under far-from-equilibrium conditions. The nanolines are always parallel to the polarization of the laser radiation. Interestingly, the nanoline width and periodicity is found to be independent of laser intensity and scan rate, *i.e.*, fluence (Fig. 3(a)), with mean values of ~380 nm and ~870 nm, respectively. The width of the pattern, however, increases with incident intensity and with scan rate, and minimum achievable pattern width is 6 μm for 11 μm spot size, as shown in Fig. 3(b). The minimum peak intensity is estimated to be ~0.1 TW/cm^2.

The structures created by this method have remarkable properties (Fig. 4). For example, when the beam is scanned twice over the same location with perpendicular polarizations, a mesh pattern is created. When the beam is scanned twice with the same polarization, the original pattern is preserved with no deformation, rather getting interlaced. If circular polarization is used, nanocircles are formed. Most remarkably, when the beam is scanned multiple times with lateral offsets, the patterns are stitched together. This way, arbitrarily large areas can be covered. During each pass, the beam scans 1 mm total distance.

In conclusion, we demonstrate highly repeatable nanoscale patterns composed of (rutile) TiO_2 nanolines or nanocircles, depending on laser polarization, on Ti surface by femtosecond laser irradiation from an all-fiber-integrated amplifier operating at 1 MHz. Remarkably, while Ti is transformed into TiO_2 at a given spot, 200 nm next to it the Ti surface remains unscathed, even though for each spot, > 1 million pulses are incident. Independent structures can be stitched if partially overlapping, similar to crack propagation. The mechanism is clearly nonlinear, indicated by the existence of a sharp intensity threshold. It can likely be understood as spontaneous pattern formation under strongly non-equilibrium conditions. Our efforts focus on understanding the exact mechanism through which these structures are created. It is seen to have distinctly different features compared to previous reports of laser-induced nanostructures. TiO_2 is technologically a very important material, with uses including molecular electronics, *e.g.*, TiO_2 is crucial for the recently discovered memristors [5] and as a photocatalyst [6]. The capability to create, and cover arbitrarily large areas, highly repeatable nanostructures made of TiO_2 (semiconducting) on Ti (metallic) surfaces is likely to have important applications in nanoelectronics.

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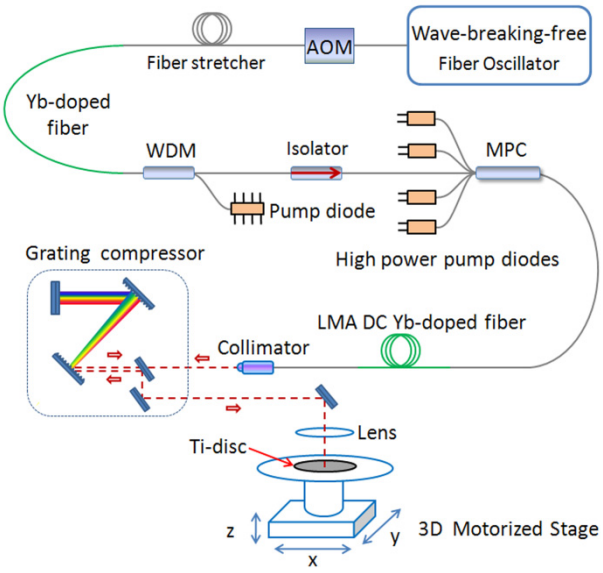

Fig. 1. Schematic diagram of the experimental set-up.

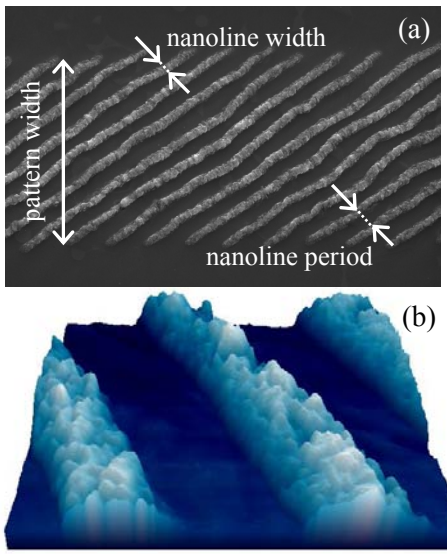

Fig. 2. (a) SEM and (b) 2x2 μm^2 AFM images of nanolines formed with at 95 mW of incident average power.

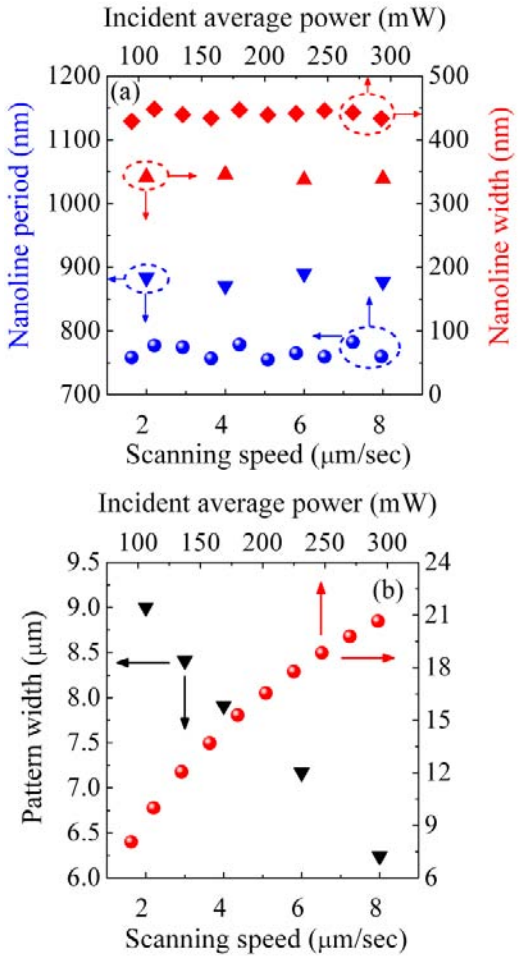

Fig. 3. (a) Nanoline periodicity and width variation, (b) pattern width variation with scan speed (at fixed power of 95 mW) and incident average power (at fixed speed of 3 μm/s). Blue circles (red diamonds) are shifted down (up) by 100 nm (50 nm) for clarity.

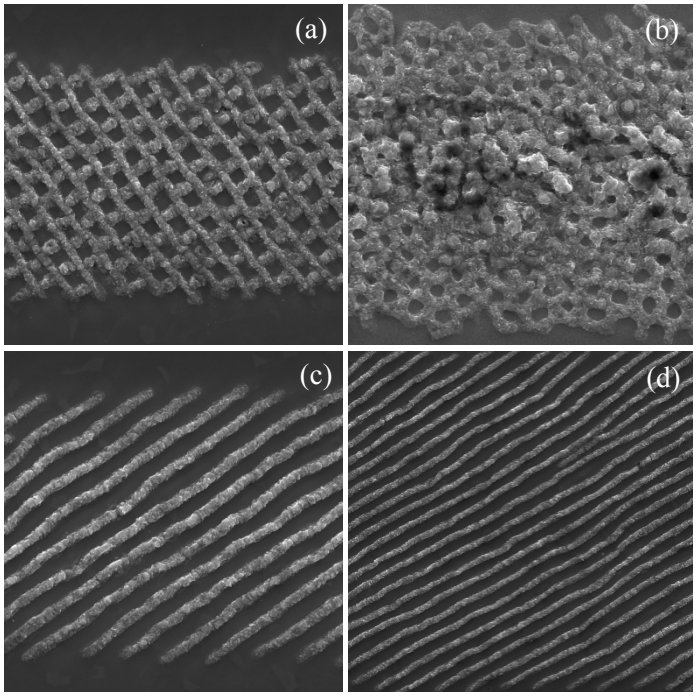

Fig. 4. SEM images of titanium dioxide nanopatterns formed on titanium surface: (a) mesh-wire structure created by double-pass with 90°-rotated polarization, (b) nanocircles created by circularly polarized light, (c) double-pass with same polarization, showing the permanence of the structures, (d) structure showing that lines from multiple, partially overlapping passes can be stitched to form a structure of arbitrarily large area.

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