Influence of Femtosecond Laser Wavelength and Ambient Environment on Morphology and Chemical Composition of Laser-Induced Periodic Structures on Metal Films

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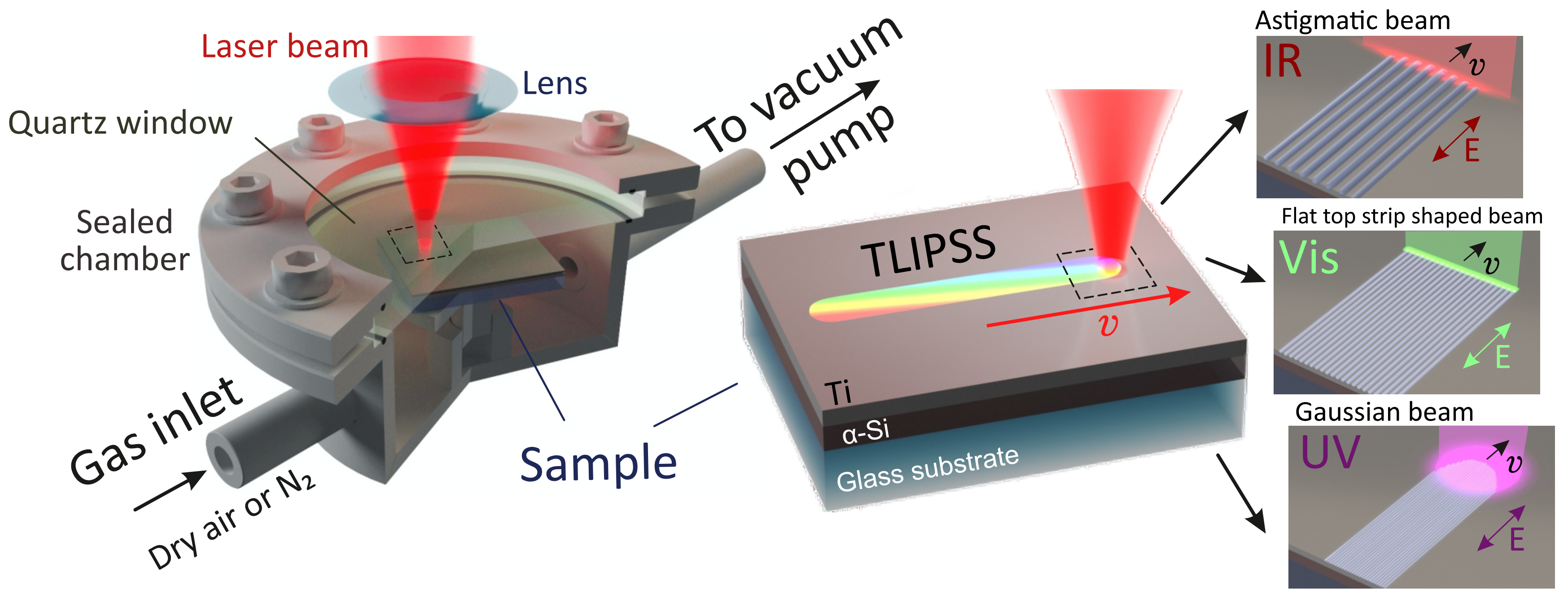
Introduction

Laser-induced periodic surface structures (LIPSS) are a periodic relief modulation that forms on the surface of solids upon the impact of high-energy laser radiation [1]. In addition to the more investigated LIPSS formed through ablation of irradiated material, there is another type of LIPSS formed due to thermally stimulated chemical reaction of a material with ambient enviroment - thermochemical LIPSS (TLIPSS). Interference between incident light and the wave scattered from surface defects is used to explain the TLIPSS formation [2]. It creates the periodic temperature distribution on the surface, which regulates thermochemical reaction. Owing to extermely high uniformity achievable with fs near-IR laser pulses, possibility to cover indefinetely large areas by lateral scanning and relative simplicity of a single-step process, TLIPSS are promising in various practical application. In this work, thermochemical LIPSS were formed on titanium films upon fs-laser irradiation with near-IR (1026 nm), visible (513 nm) and UV (256 nm) wavelengths. To study the influence of the ambient enviroment on both morphology and chemical composition, experiments were carried out in the air, vacuum and nitrogen-rich atmosphere, when using near-IR pulses.

Experimental setup



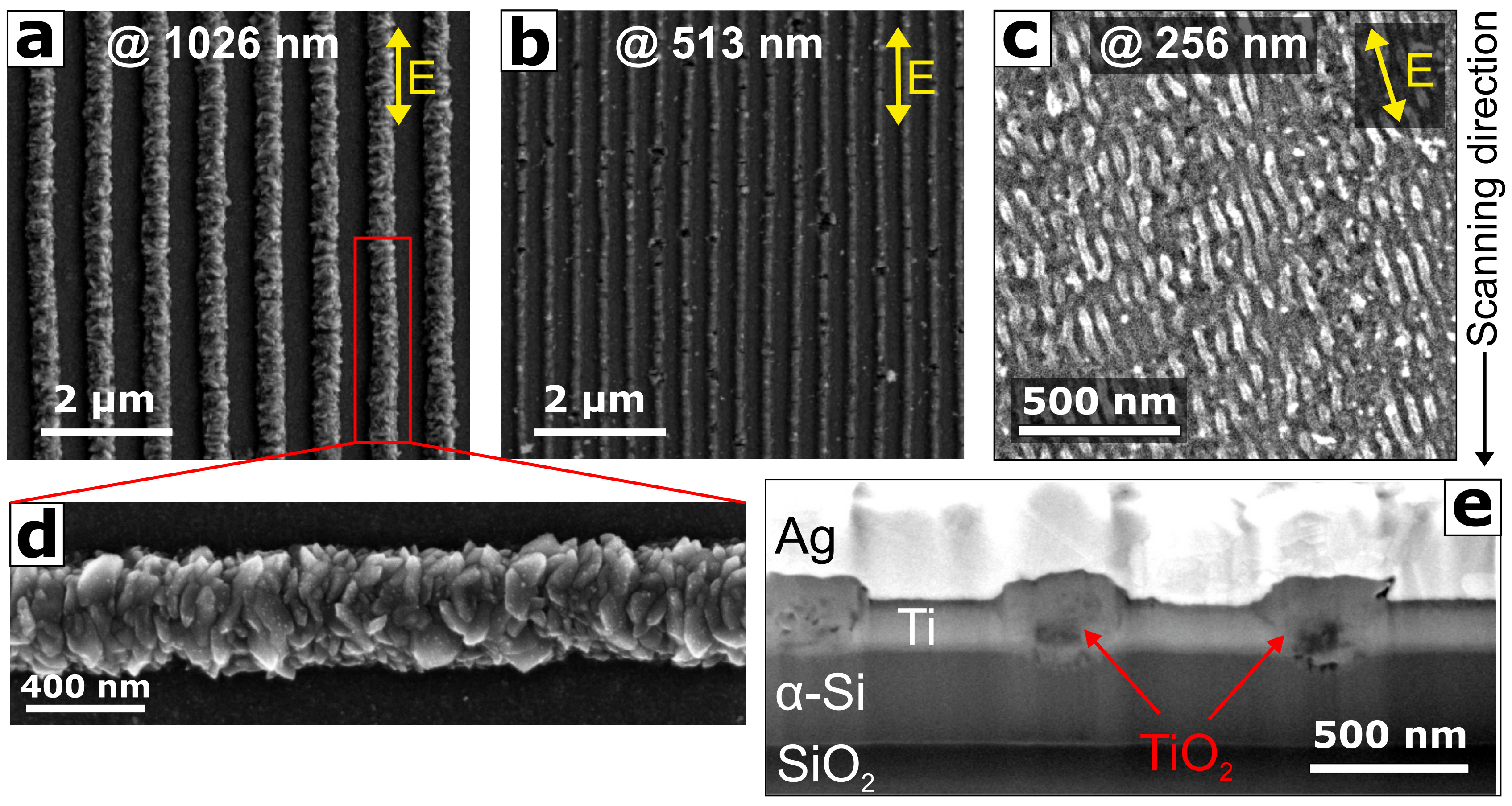
Femtosecond laser:
Pharos 6W (Light Conversion Ltd)
λ = 1026, 513, 256 nm, t_p = 232 fs
f = 50-200 kHz

Beam shapes:
- Astigmatic Gaussian: ~150x15 μm @ 1026 nm
- Flat-top stripe-shaped: 30x1 μm @ 513 nm
- Gaussian: 2 μm @ 256 nm

Samples used in the experiments were a two-layer Ti/α-Si film with Ti being the top layer with a thickness of 90 or 180 nm produced by magnetron sputtering on a glass substrate. An intermediate 250 nm thick a-Si layer was introduced to avoid possible migration of oxygen from the glass substrate.

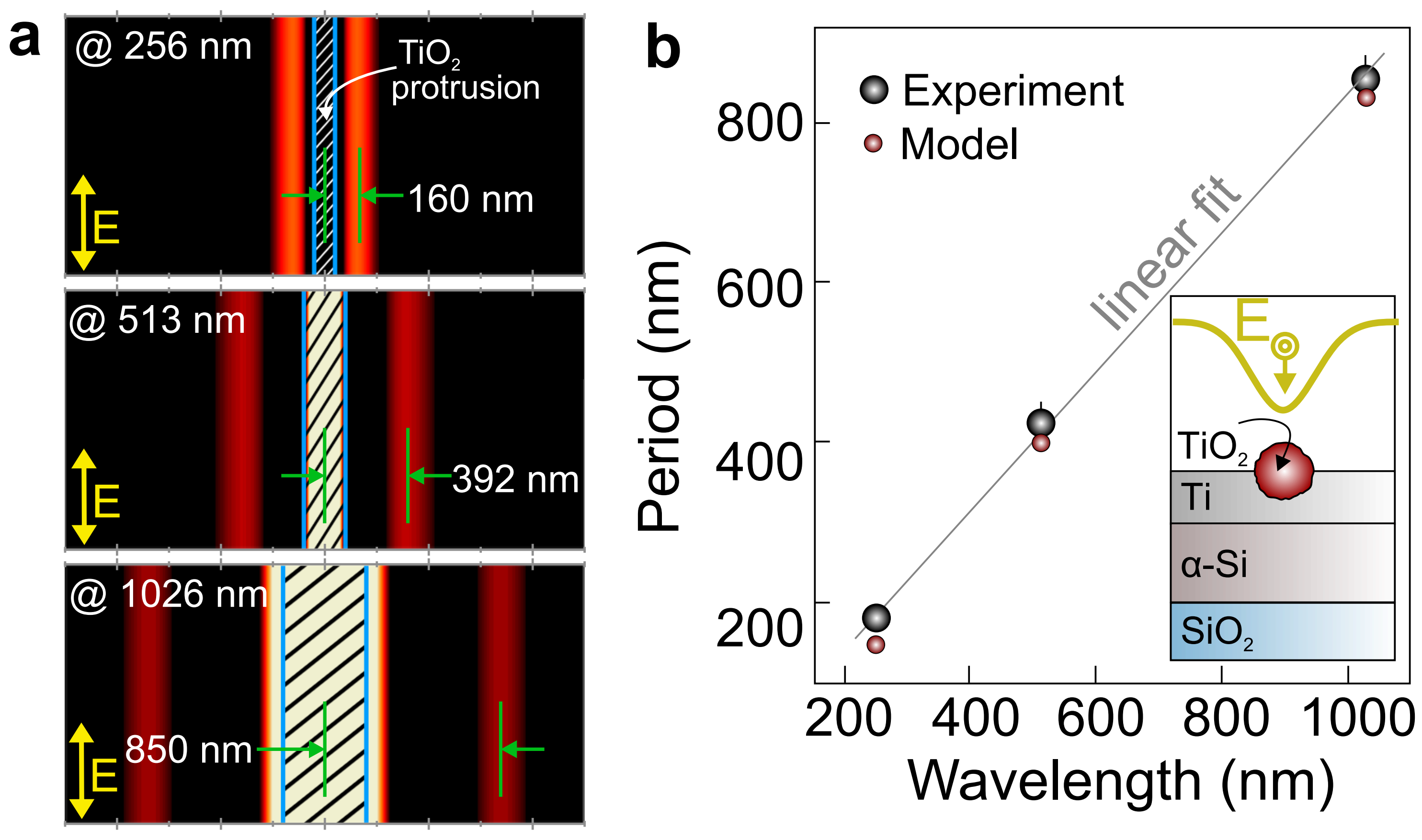
Experimental results

The highly regular TLIPSS have been formed on 90 nm thick Ti film upon near-IR laser radiation (λ = 1026 nm, F = 90 mJ/cm^2, υ = 1 μm/s) in air environment. The TLIPSS are oriented along the polarization direction of incident laser radiation and have a period of 853±20 nm. Each protrusion has a width of ≈400 nm and consists of TiO_2 nanocrystallites with random orientation. The TiO_2 starts to grow from the Ti film surface as a result of thermochemical interaction with oxygen. Formed protrusion occupies a larger volume in comparison to intact film due to the porous structure of rutile nanocrystals and a large Pilling and Bedworth ratio R_{PB} = 1.78 for titanium and its oxide. When utilizing second-harmonic (λ = 513 nm) radiation, highly uniform TLIPSS were formed having a period of 416±17 nm at υ = 3 μm/s and F = 50 mJ/cm^2. The rutile protrusions show smoother surface morphology in comparison to the morphology of the TLIPSS produced with near-IR laser pulses.



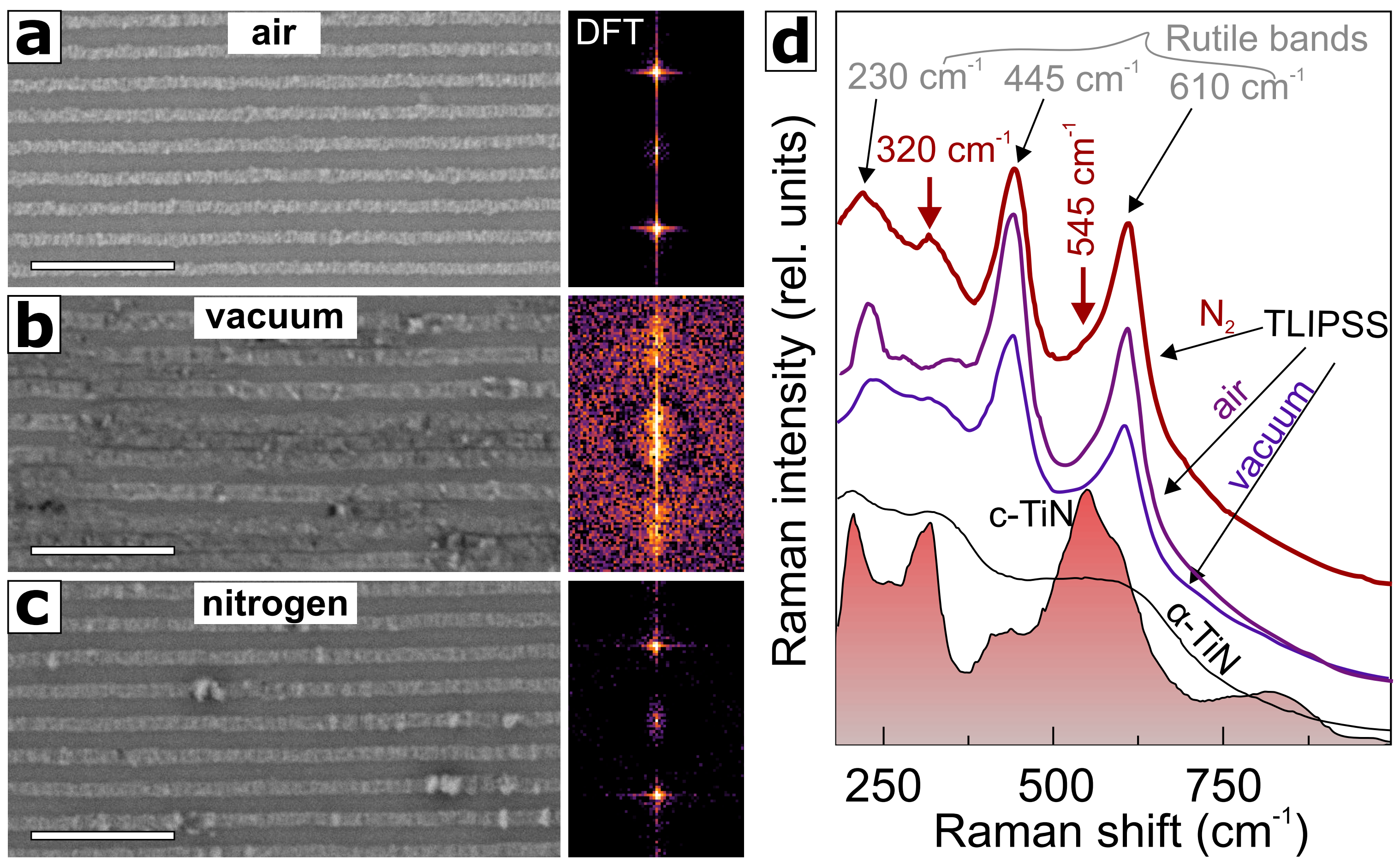
Top-view SEM images of TLIPSS structures produced on the 90-nm thick Ti film in air at (a) λ = 1026 nm, (b) λ = 513 nm, (c) λ = 256 nm. A double arrow shows the polarization direction. (d) The enlarged view of the single TiO_2 protrusion. (e) SEM image of a cross-sectional FIB cut made perpendicularly to the TLIPSS orientation (structures formed at λ = 1026 nm).

Fourth-harmonic (λ = 256 nm) laser pulses were used to further reduce the TLIPSS period. The formation of the structures with the period of 182±22 nm is shown at maximal available laser fluence F = 35 mJ/cm^2 and scanning speed of υ = 1 μm/s. The averaged TLIPSS period scales linearly with the wavelength of the incident laser radiation. To explain this dependence, we performed finite-element frequency-domain simulations of the scattering of a linearly polarized wave from an isolated TiO_2 protrusion as illustrated in the inset in figure. The geometry of the protrusion as well as optical properties of TiO_2 (including the influence of the porous structure) at different wavelengths were taken into account. The results show a good match with the experimental values confirming the electromagnetic origin of the TLIPSS ordering.



(a) 2D intensity profiles calculated near the Ti surface containing the central TiO_2 protrusion at different incident laser wavelengths. Shaded rectangles indicate the area occupied by the protrusion. (b) Measured and calculated averaged TLIPSS period vs. incident laser wavelength. Inset shows schematic illustration of the modeled geometry.

To study the influence of the ambient atmosphere on the formation of the TLIPSS protrusions, the following processing parameters have been chosen: f = 200 kHz, F = 70 mJ/cm^2, υ = 1 μm/s. The TLIPSS regularity worsens in a vacuum, while additional protrusions are formed between the primary ones, which appears as noise on a 2D-DFT map. The TLIPSS formed in the nitrogen-rich atmosphere have a similar period (≈940 nm) and better ordering. Raman spectra averaged over multiple surface areas of the produced TLIPSS revealed several bands appearing at 230, 320, 445 and 610 cm^{-1}. They indicate characteristic vibration modes of TiO_2 rutile (except band at 320 cm^{-1}). It suggests that oxidation dominates in the formation process even for TLIPSS produced in the nitrogen-rich atmosphere. The line at 320 cm^{-1} is attributed to TiN, which can be seen from the reference Raman spectra of crystalline TiN as well as its amorphous phase.



SEM images of the TLIPSS formed on the 180-nm thick Ti film in air (a), vacuum (b) and nitrogen-rich atmosphere (c). Insets show 2D-DFT (discrete Fourier transform) images. (d) Averaged Raman spectra of the TLIPSS produced in the different ambient environments.

Conclusion

TLIPSS with periodicity of ≈850, 420 and 180 nm were fabricated on Ti thin films using near-IR, visible and UV radiation. The linear dependence of the period on irradiating wavelength is demonstrated supported by the numerical simulations. It's shown that the ambient enviroment influences regularity of the obtained TLIPSS as well as their chemical composition. Raman spectroscopy revealed complex TiN/TiO_2 composition with dominating TiO_2 (rutile) component for TLIPSS produced in the nitrogen-rich atmosphere. *Further details can be found in the paper* [3].

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