Femtosecond LIPSS on indium-tin oxide thin films at IR wavelengths

Balázs Bánhegyi\textsuperscript{a,b*}, László Pétera, Péter Dombi\textsuperscript{a,c}, Zsuzsanna Pápa\textsuperscript{a,c}

a. Wigner Research Centre for Physics, Konkoly-Thege Miklós út 29-33, 1121 Budapest, Hungary; b. Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, 1111 Budapest, Hungary; c. ELI-ALPS, ELI-HU Nonprofit Kft., Wolfgang Sandner utca 3, 6728 Szeged, Hungary

ABSTRACT

In our work we focused femtosecond laser pulses in the infrared region onto conducting indium-tin-oxide (ITO) thin films. We observed laser induced periodic surface structures (LIPSS) with increasing periodicity close to $\lambda/10$ scaling. We conducted supporting finite-difference time-domain calculations to investigate the origin of these morphologies. The results suggest that the surface forms are rooted in the field localization in the surface pits leading to a periodically increased absorption of the laser pulse energy that creates the observed periodic structures.

Keywords: LIPSS, femtosecond, light-matter interaction

1. INTRODUCTION

Indium-tin-oxide (ITO) is one of the most widely used conducting oxides due to its high electrical conductivity and broad spectral transmission from the visible to the infrared range. Deposited in the form of thin surface film, it can serve as a transparent electrode or conductive layer in nanophotonic experiments\textsuperscript{1}, electrochemical systems\textsuperscript{2}, photovoltaic devices\textsuperscript{3-5}, or even biosensors for virus detection\textsuperscript{6}. Previously it was shown that the surface of an ITO thin film can be patterned with ultrashort laser pulses and certain characteristics of the treated areas can be altered. Many of these comparative studies investigated the laser-induced periodic surface structure (LIPSS) generation both experimentally and theoretically.

In general, LIPSS formations can be divided into two categories based on their periodicity compared to the laser wavelength. i) In the case of low-spatial-frequency LIPSS (LSFL), the laser wavelength and the periodicity of the generated structures are on the same order of magnitude and the orientation of the structures can be either parallel or perpendicular to the laser polarization. ii) The periodicity of the high-spatial-frequency LIPSS (HSFL) is considerably smaller than the applied laser wavelength, and these structures are usually perpendicular to the laser polarization\textsuperscript{7}. The formation mechanism of LIPSS generated by ultrafast laser pulses with different wavelengths and pulse durations has been extensively examined in recent years. It is generally accepted that the perpendicular LSFL generation on materials with large electron concentration is caused by the interaction of the incident laser field and the electromagnetic wave on the surface scattered by the initially rough surface\textsuperscript{8-10}. The interference of these waves distorts the spatial field distribution along the surface, thus forming a periodic intensity pattern that leads to the corresponding ablation. LSFL with parallel orientation is mainly observed on dielectrics due to a specific nonpropagating electromagnetic mode close to the rough surface (radiation remnants)\textsuperscript{7,11}. On the other hand, explaining the emergence of HSFL patterns and their periodicities is more challenging. Previously it was proposed that the interference of the incident laser radiation with the excited sub-wavelength surface plasmon polaritons could be responsible for the formation of periodic sub-wavelength ripples\textsuperscript{12}.

*banhegyi.balazs@wigner.hu
2. EXPERIMENTAL SETUP AND METHODS

In our experiments, we used a regenerative Ti:sapphire amplifier (Coherent Legend Elite) seeded with a home-built oscillator. The 800 nm, 50 fs output pulses with 10 kHz repetition rate were directed into an optical parametric amplifier (OPA) with a 70-fs output pulse length, and controllable output wavelength between 300 nm and 15 µm. The sample was a 150 nm thick ITO layer deposited onto a 1 mm fused silica substrate. These infrared pulses were focused by back-illumination to the ITO-glass interface by a 200 mm focal length CaF2 lens, resulting a focal spot with 260 µm diameter. All LIPSS generation experiments were conducted in ambient air environment. Pulse energies were controlled by a set of discrete neutral density filters. The laser-treated areas and the formed LIPSSs were inspected with a scanning electron microscope (TESCAN MIRA3 SEM). To resolve the surface morphology, the in-beam secondary electron detector was chosen with 5 kV accelerating voltage. The images were acquired via line accumulation with a 4-mm working distance and a magnification between 2400 and 160 000. To gather information about the composition and to examine the amount of ITO ablated from the surface, we also performed element analysis in the laser-treated areas. Before the LIPSS experiments, the surface of the original, untreated ITO layers was also investigated with a PSIA XE-100 atomic force microscope in dynamic, non-contact mode over 5 μm × 5 μm and 20 μm × 20 μm scanning areas. The average roughness was determined by the manufacturer's (XEI) software.

![Experimental setup with femtosecond light source (LS), tunable optical parametric amplifier (OPA), programmable shutter (SH), neutral density filter (ND), focusing lens (L), ITO covered glass sample (S) and CCD camera (C). Inset: back-illumination focusing geometry with normalized electric field distribution and infrared spectra of the laser pulses at the applied wavelengths.](image)

3. RESULTS AND DISCUSSION

3.1 HSFL structures

Focusing first on the HSFL structures, their properties can be analyzed in more detail by taking a closer look the illuminated spots. The generated HSFL formations for all three wavelengths are shown in Figs. 2(a-c) with higher magnification. Fig. 2(d) shows the deduced periodicities. The periodicity of the HSFLs was calculated by applying a 2-dimensional fast Fourier transform (FFT) to the SEM images. Based on the FFT inverse-space spectra, the periodicity of the HSFLs is between 150 and 300 nm, with a slight increase for larger wavelengths (Fig. 2(d)).
Figure 2. Detailed SEM images of the HSFL formations in case of a) 1.6 µm and 3.8 × 10¹¹ W/cm², b) 2.0 µm and 2.3 × 10¹¹ W/cm², c) 2.4 µm and 2 × 10¹¹ W/cm² peak intensity pulses. Inset figures show the FFT inverse-space spectra of the SEM images unveiling real space periodicity. d) Period length values with error bars calculated based on the distribution of FFT spectra.

These structures having period lengths much smaller than the wavelength and perpendicular orientation can be discussed in the frame of electromagnetic simulations, where they are often called r-type LIPSS¹³⁻¹⁵. This means that they are connected to the initial roughness of the surface. To check this explanation, we took into account the roughness of the ITO layer, which was studied with an atomic force microscope (AFM) before any LIPSS experiment took place. Although the average roughness is not very high (rms roughness < 5 nm), the microroughness of the surface has a similar characteristic length to the period of the observed LIPSS structure.

Based on the electromagnetic theory, the interaction of the incident light with the initial structure of the irradiated material can lead to field localization in the pits of the rough surface. These pits of the surface may act as seeds for the more prominent structural changes or even material removal¹⁶. To investigate the possible field localization, we calculated the distribution of the electric field inside the ITO with Lumerical FDTD Solutions software. We can get an indication of the roughness-based origin of the observed structures if we plot the field distribution maps recorded in the top 10 nm depth of the layer. These averaged electric field patterns belonging to the applied wavelengths (1.6 µm, 2.0 µm, and 2.4 µm) are plotted in Fig. 3 (a-c) (values are normalized). These figures can indicate the formation of the HSFL structures since the spatial domains exhibiting the largest local fields correspond to the structures of the rough surface. Furthermore, if the electric field pattern is Fourier-transformed, the vertical orientation of the high-intensity domains is clearly visible (note the bright areas located along the horizontal axis in the insets of Fig. 3(a-c)). The periodicity of the brightest vertical domains is the smallest for 1.6 µm, varying between 180 and 400 nm, while for the other two wavelengths it is slightly larger (190-430 nm for 1.6 µm and 200-500 nm for 2.4 µm) matching nicely to the slight wavelength dependence of the periodicity of the LSFL structures (c. f. Fig. 2(d)). Furthermore, if we compare our data with the literature results of ITO patterning, we can experience that despite the diverse experimental conditions of previous studies and our investigations, the appearing HSFLs have very similar properties regarding both the orientation and the periodicity. This also suggests that it is more likely the ITO itself (and its properties) that determines the structure formation, and the wavelength/duration of the applied laser pulses has less impact.
3.2 LSFL structures

Concentrating onto the LSFL structures appearing at 2 and 2.4 µm wavelength, it is important to mention that the parallel orientation of LSFL structures is not characteristic of conductive layers. To gather more information about the formation of these surface structures, we performed element analysis around the laser-treated areas. A 10 kV electron accelerating voltage was used for the sake of achieving a sufficient X-ray yield for all EDS lines (that all lie in the < 4 keV regime) and to keep the incidence depth of the electron beam relatively low. The typical excitation volume under the above-mentioned circumstances is around 0.2 µm$^3$, which means that the composition information is averaged over this volume. Taking into account the limit above, we performed a line scan on the structured area generated by illuminating the sample 1 s with 2.4 µm wavelength, $2 \times 10^{11}$ W/cm$^2$ peak intensity pulses.

![Figure 4](image)

Figure 4. a) Element analysis results obtained by a line scan on the laser treated area. The dashed blue line shows the line path. b) Tilted SEM image of the HSFL formations of the ITO and the structured underlying glass generated with 2.4-µm wavelength, $2.3 \times 10^{11}$ W/cm$^2$ peak intensity pulses with 1 s illumination. c) Local composition of the different components on the surface along the scan line.

Figure 4. shows the line scan path and the obtained relative density of elements along the scan based on the detected electrons originating from the listed shells. Approaching the center of the focal spot, the Si concentration starts to oscillate as the ITO becomes periodically ablated and the underlying glass becomes uncoated. At the same time, in an opposite phase, the In and Sn concentrations also oscillate showing the same effect. This clearly shows that LSFL structures form through this periodic ablation of the ITO layer. This means that there must be a periodically larger local field that promotes the ablation. The physical origin of this periodic ablation is still an open question. The orientation and periodicity of the LSFL can be related to non-metallic surfaces, which hints that these structures may origin from a periodic intensity pattern developing on the substrate surface [11]. However, since the optical properties of fused silica...
are almost constant between 1.6 and 2.4 µm, it is expected that LSFL should appear at all illumination wavelengths, which is not the case.

4. CONCLUSIONS

We performed experiments in which we used femtosecond pulses in the infrared region with three different wavelengths to generate LIPSS on an ITO thin film. We observed primary HSFLs with periodicity between 150 and 300 nm with an orientation perpendicular to the laser polarization. The much smaller periodicity compared to the wavelength can be interpreted as a roughness-dependent structure. FDTD simulations based on AFM measurements were conducted, that confirmed our hypothesis about the origin of the LIPSS formations. We concluded that the initial surface roughness of the ITO layer and the field localization in the pits lead to a periodic absorption of the laser pulse energy that creates the periodic structures and even periodic material ablation from the substrate. We also obtained LSFLs parallel to the laser polarization with 2 µm periodicity, which we investigated with element analysis unfolding the periodic concentration of the surface material components.

REFERENCES

[1] Kanehara, M., Koike, H., Yoshinaga, T. and Teranishi, T. Indium Tin Oxide Nanoparticles with Compositionally Tunable Surface Plasmon Resonance Frequencies in the Near-IR Region. Journal of the American Chemical Society 131, 17736-17737 (2009) https://doi.org/10.1021/ja9064415

[2] Sakamoto, K., Kuwae, H., Kobayashi, N., Nobori, A., Shoji, S. and Mizuno, J. Highly flexible transparent electrodes based on mesh-patterned rigid indium tin oxide. Scientific Reports 8, 2825 (2018) https://doi.org/10.1038/s41598-018-20978-x

[3] Jahng, W. S. and Francis, A. H. Is indium tin oxide a suitable electrode in organic solar cells? Photovoltaic properties of interfaces in organic p/n junction photodiodes. Applied Physics Letters 88, 093504 (2006) https://doi.org/10.1063/1.2180881

[4] Al-Ibrahim, M., Roth, H. K. and Sensfuss, S. Efficient large-area polymer solar cells on flexible substrates. Applied Physics Letters 85, 1481–1483 (2004). http://doi.org/10.1063/1.1787158

[5] H. Liu, and R. Sun. Laminated active matrix organic light-emitting devices. Applied Physics Letters 92 063304 (2008). https://doi.org/10.1063/1.2844854

[6] Guo, D., Zhuo, M., Zhang, X., Xu, C., Jiang, J., Gao, F., Wan, Q., Li, Q. and Wang, T. Indium-tin-oxide thin film transistor biosensors for label-free detection of avian influenza virus H5N1. Analytica Chimica Acta 773, 83–88 (2013) https://doi.org/10.1016/j.aca.2013.02.019

[7] Bonse, J., Höhm, S., Kirner, S. V., Rosenfeld, A., and Krüger, J. Laser-Induced Periodic Surface Structures - A Scientific Evergreen. IEEE JOURNAL OF SELECTED TOPICS IN QUANTUM ELECTRONICS 23, 9000615 (2017) http://doi.org/10.1109/JSTQE.2016.2614183

[8] Young, J. F.,Preston, J. S., van Driel, H. M. and Sipe, J. E. Laser-induced periodic surface structure. II. Experiments on Ge, Si, Al, and brass. Physical Review B 28, 1155-1172 (1983) http://doi.org/10.1103/PhysRevB.27.1155

[9] Dufft, D., Rosenfeld, A., Das, S., K., Grunwald, R., and Bonse, J.. Femtosecond laser-induced periodic surface structures revisited: A comparative study on ZnO. Journal of Applied Physics 105, 034908 (2009) https://doi.org/10.1063/1.3074106

[10] Bonch-Bruevich, A. M., Libenson, M., N., Makin, V., S. and Trubaev, V. V. Surface electromagnetic waves in optics. Optical Engineering 31, 718 (1992) https://doi.org/10.1117/12.56133
[11] Sipe, J. E., van Driel, H. M., and Young, J. F. Surface electrodynamics: Radiation fields, surface polaritons, and radiation remnants,” Can. J. Phys. 63 104–113 (1985) https://doi.org/10.1139/p85-017

[12] Wang, L., Cao, X.-W., Abid, M.-I., Li, Q.-K., Tian, W.-J., Chen, Q.-D., Juodkazis, S., and Sun, H.-B. Nano-ablation of silica by plasmonic surface wave at low fluence, Optics Letters 42, 4446 (2017) https://doi.org/10.1364/OL.42.004446

[13] Skolski, J. Z. P., Römer, G. R. B. E., Vincenc Obona, J., and Huis in ’t Veld, A. J. Modeling laser induced periodic surface structures: Finite-difference time-domain feedback simulations. Journal of Applied Physics 115, 103102 (2014) http://dx.doi.org/10.1063/1.4867759

[14] Dëziel, J-L., Dumont, J., Gagnon, D., Dubé, L. J., Messaddeq, S. and Messaddeq, Y. Toward the formation of crossed laser-induced periodic surface structures. Journal of Optics 17, 075405 (2015) https://doi.org/10.1088/2040-8978/17/7/075405

[15] Rudenko, A., Colombier, J-P., Höhm, S., Rosenfeld, A., Krüger, J., Bonse, J. and Itina, T. E. Spontaneous periodic ordering on the surface and in the bulk of dielectrics irradiated by ultrafast laser: a shared electromagnetic origin. Scientific Reports 7, 12306 (2017) http://doi.org/10.1038/s41598-017-12502-4

[16] Pan, A., Wang, W., Liu, B., Mei, X., Yang, H. and Zhao, W., Formation of high-spatial-frequency periodic surface structures on indium-tin-oxide films using picosecond laser pulses. Materials & Design 121, 126–135 (2017) https://doi.org/10.1016/j.matdes.2017.02.055