Thesis Changes Log

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PhD Program: Physics

Title of Thesis: Aspects of laser-induced structuring and surface modification of technologically significant metal and semiconductor materials

Supervisor: Prof. Sakellaris Mailis

The thesis document includes the following changes in answer to the external review process.

I am very grateful to the reviewers for their detailed study of my work and provided suggestions. Below are my point-to-point replies and corresponding changes of the Thesis text.

Prof. Sergey Alyatkin

- *The title is extremely broad… therefore, I would recommend to "narrow" the title and make it more specific.*

A new version of the title is proposed: "Aspects of laser-induced structuring and surface modification of technologically significant metal and semiconductor materials".

- *Too general and vague wording: … both novel materials and especially 2D materials are wide terms, used in different context by specialists working in different fields*

The novel materials in question were named in the revised version (Abstract, p. 3):
"Discoveries in novel materials (namely, transitional metal dichalcogenides (TMDCs) and porous silicon) and characterization techniques…"

- *Too general and vague wording: … "some aspects of material modification" should be replaced with precise description of the research directions pursued*

The research directions pursued were formulated in a more precise manner in the revised version (Abstract, p.3):
"This research was aimed, in particular, at characterizing topographical, structural and chemical changes occurring in a selection of materials under pulsed laser scanning and continuous wave (non-pulsed, c.w.) laser scanning in context of developing simple methods of surface modification."

- *Too general and vague wording: … "For higher fluences, self-assembled conical structures are formed, reaching heights of 30 μm." It would be good to understand what is meant here with "higher"*

The vague mention was clarified in the revised version (Abstract, p.4):
"For irradiation protocols that combine several repetitions of the scanning pattern and fluences above 13 J/cm2,, self-assembled conical structures are formed, reaching heights of 30 μm."

- *Too general and vague wording: … "Lasers are widely used in industrial material processing [1]. Compared to other methods of material processing, they possess several key benefits". The thesis would benefit from indicating these "other methods of materials processing."*

A selection of methods against which direct laser writing surface treatments can be reasonably compared was given in the revised version (Chapter 1.1, p. 20):
"Lasers are widely used in industrial material processing [1]. Compared to other methods of material processing, such as mechanical machining [2], chemical milling [3], electrochemical machining [4], electrical discharge machining [5] etc. they possess several key benefits…"

- *Too general and vague wording: … "A sufficiently short pulse excites a large amount of electrons at time scales much shorter than those required to heat up the ion lattice." What is this time? How the time scale changes when matter changes (I believe this time should be indicated at least for the type of materials investigated here - GaAs, 2D TMDCs)*

Sections dedicated to absorption and relaxation of ultrashort pulses were added in the revised version

(Chapters 1.2.2-1.2.4). Additionally, examples of electron thermalization and electron cooling time scales for materials such as GaAs, Al, Si and MoS2were provided. (Chapter 1.2.4 Relaxation of ultrashort pulses).

- *Too general and vague wording: ... "By using pulsed irradiation, it is easier to reach peak beam intensities that surpass energy thresholds needed to ablate, melt or oxidize the material." Please provide these numbers or range of numbers*

The question of ultrashort pulse thresholds for ablation and melting was addressed in Chapter 1.2.4 in the revised version. Relaxation of ultrashort pulses, with example numbers provided.

- *The Introduction section lacks underlying physics and phenomena: ... According to the dissertation, the LIPSS is known for 6 decades and has been observed in numerous materials. This hints us that the mechanism is well understood and as a reader I expected to see the description*

The Chapter 1.3.2 was added in the revised version, addressing the multitude of existing theories on LIPSS phenomena.

- *The Introduction section lacks underlying physics and phenomena: ... Here the question immediately arises whether LIPSS is possible in polished samples?*

The influence of surface roughness was addressed specifically in the revised version (Chapter 1.3.2, p. 36):
"Typically, for polished surfaces [53] and deposited films of low (<5 nm) roughness [71] those factors are taken to be F=0.1 (low roughness) and s=0.4 (spherically shaped islands). Indeed, LIPSS are observed on polished surfaces. Imprinting a periodic structure is possible even with a single pulse [72]; however, to observe well-defined LIPSS a multitude of pulses [61] or c.w. irradiation are required."

- *General note on low quality of Figures reproduced from other works (as an example, Fig3 at p.39). Another thing is their high fraction compared to original number of figures made by Igor for the thesis."*

The Figure in question was remade in improved quality in the revised version (Chapter 1.4.9, p. 69). Additional original figures were produced for Chapters 3 and 4. Perhaps there has been some confusion as I have been citing my own papers in the captions of numerous figures that appear in this thesis. It worth noting that the figures reproduced from these published papers were also made by me. For clarity, I have now removed all the self-referencing from the figures.

- *I would like to pay attention to personal contribution sections... the way how it is currently presented leaves an impression that personal contribution of Igor is relatively small (which I am sure is a wrong). See as an example p.42-43, p.82.*

The personal contributions sections in question were reworked (Chapter 2.1, Chapter 3.1).

- *I have a question regarding leading role of candidate in publication #4: Averchenko AV, Salimon IA, Zharkova EV, Lipovskikh S, Somov P, Abbas OA, Lagoudakis PG, Mailis S. Laser-enabled localized synthesis of Mo1-xWxS2 alloys with tunable composition. Materials Today Advances. 2023 Jan;17:100351..*

I was a coauthor in this publication. After clearing out some confusion, this publication was removed from the list of publication on which the thesis is based. The thesis is not focused on these results, and they are only brought up as context when relevant.

Finally, I would like to thank Prof. Sergey Alyatkin for a useful and insightful discussion.

Prof. Vasileios Apostolopoulos

- *What is the industry standard used at the moment to modify and structure GaAs?*

This question was addressed in the revised version in Chapter 1.3.6, p. 44:
"The established industry standard for creating GaAs chip devices (for example, mobile phones [108]) is using techniques such as metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) [108]."

- *Are there processes where Laser writing is used to modify or structure GaAs in research or industry?*

This question was addressed in the revised version in Chapter 1.3.6, p. 45:
"Lasers are used in GaAs modification and structuring mainly in the DLIP method, allowing to deposit ordered arrays of quantum dots during under an arsenic flux [120] or to induce a pattern of nanoholes via using a positive UV photoresist [121]. Alternatively, LIPSS patterning was suggested for creating anti-reflective coatings on GaAs [122]."

- *What exactly was the wafer used for the experiments… it would be useful to know if the GaAs is semi-insulating, undoped, doped and specify the method of growth and supplier.*

This question was addressed in the revised version in Chapter 2.3.1, p. 74:
"The sample used in our experiments was a section of an undoped semi-insulating GaAs (100) wafer with a thickness of 0.5 mm that was supplied by our collaborators. Such high quality wafers are used for MBE growth of semiconductor microcavities."

- *Also, I would like to know how do you think that different compositions would affect your findings?*

This question was addressed in the revised version in Chapter 2.3.5, p. 90:
"We anticipate that the oxidation process is dependent on the doping of GaAs in a way similar to anodic electrochemical oxidation [198] or liquid phase chemical enhanced oxidation [119], where the process depends on the hole concentration…"

- *In chapter 3 you write "The resulting nanoribbon arrays exhibit enhanced persistent photoconductivity, and their photocurrent increased by three orders of magnitude compared to their continuous film counterparts." Could you state of what applications could benefit from this, and maybe include some references with devices of TMDs that use photoconductivity.*

This question was addressed in the revised version in Chapter 1.3.8, p. 50:
"While high response times are not desirable for every application (in typical and wide-spread building monitoring photodiodes may be preferred over photoresistors [44]), there is interest in materials that exhibit "persistent photoconductivity" (PPC) [145, 142, 146, 147]. Elements that retain photocurrent over a prolonged time allow to avoid reacting to fluctuations, and there is a growing interest [148] in applications of PPC in optical memory [149], charge storage [150], solar cells [151] and simulation of neurotypical devices [152]."

- *More a comment rather than a question but a demonstration for an application for example by measuring reflectivity in an irradiated area would be I think useful.*

Thank you for this suggestion.
I have indeed noticed that the laser-irradiated tracks that exhibit submicron microstructuring exhibit also high scattered reflection. This fact was very convenient throughout experiments, allowing to distinguish structured films from uniform ones by dark field optical microscopy with just an x20 magnification.
However, I attribute this change in reflectivity mainly to the structural change; the focus of the study, instead, was on the photoconductive properties of the structured films, as those properties offer a clear avenue towards applications.
Considering the reflectivity of the submicron structures synthesized would certainly be a possible future prospect.

- *What is the problem that you are trying to solve with the aluminum composite, I understand that the conical structures are poorly explained in literature but is there any other motivation.*

This question was addressed in the revised version in Chapter 2.4, p. 92:
"For the aluminum alloys in particular, there is interest in studying the corrosion mechanism to improve resistance to corrosion, including the use of laser-based methods such as laser surface melting (LSM). The introduced elemental inhomogeneity of the alloy's surface has an effect on its corrosive properties, which may be positive or negative … [128]. This emphasizes the relevance of an in-depth FIB-SEM investigation of the conical microstructures obtained through ablation."

- *In figure 14 is the view from the top or a cross-section?*

This necessary clarification was made in the revised version in the caption of Figure 19:
"Figure 19 SEM images showing appearance of ablated areas (top view)."

- *Could you give any information if there is literature working on waveguide writing in porous silicon. It fundamentally seems like a high loss material for waveguides so I would like to know what is the scope for producing integrated circuits..*

This question was addressed in the revised version in Chapter 1.3.10, p. 54:
"PorSi waveguides are widely applied in optical interference devices (e.g. tuned photodetectors [178]), particularly chemical sensing and biosensing [179,180]. Volume scattering losses in PorSi depend, naturally, on the propagating wavelength, but also on the size of the pores, possibly being as low as 10^{-3} – 10^{-2} dB/cm for pores with a low (10-20 nm) diameter [181]. Several methods of creating PorSi channel waveguides are known, such as lithography and localized laser oxidation [182,183]."
While propagation losses in porous silicon are indeed high compared to fibers used in telecommunication, we consider porous silicon waveguides in the context of creating micron-scale

sensors, for which propagation losses in porous silicon are acceptable.

Prof. Fedor Fedorov

- *I encountered a few typos that might require the author's attention.*

Thank you very much for pointing out the typos, they were corrected.

- *I would suggest to make the title of the thesis more specific.*

A new version of the title is proposed: "Aspects of laser-induced structuring and surface modification of technologically significant metal and semiconductor materials".

- *What about the anisotropic properties of materials? Can they be considered?*

This question was addressed in the revised version in Chapter 1.3.6, p. 44:
"Additionally, it is known that GaAs exhibits a notable peak of anisotropy of reflectance at ~ 276 nm [107]. At 244 nm, the difference of reflectance ΔR/R may still reach 0.001."
and in Chapter 2.3.2, p. 78:
"No evidence of anisotropy having a strong effect on formation of LSFL-II was registered. Scanning performed under various random orientations of the GaAs crystal led to similar results. It is likely that the directionality of LSFL-II formation outscales such anisotropy."

- *For the GaAs part, a comparison between reflected and adsorbed energies might be beneficial. Both melting and oxidation take place (and other processes).*

This question was addressed in the revised version in Chapter 1.3.6, p. 44:
"The refractive index of GaAs at 244 nm was measured by two-channel polarization modulation ellipsometry to be 2.063 + i * 4.052 [105], resulting in a reflectance of 68% at normal incidence. A similar precise measurement was not found for GaAs oxide obtained by UV oxidation. Anodically grown native oxide of GaAs [106] was used for comparison instead. According to this study, the oxide becomes completely opaque for wavelengths shorter than 220 nm. There does not appear to be a more detailed study of the GaAs oxide UV reflectance in the literature."

- *What is the main origin of pores?*

This question was addressed in the revised version in Chapter 2.3.5, p. 90:
"A probable reason for porosity of the oxidized layer could be sublimation of oxides of Ga and As. It is known that at temperatures above 440 °C the Ga2O suboxide becomes volatile, with its sublimation forming pits up to 11 nm deep, thermally inducing substantial mass transport [199]. Growth of larger pores could be promoted by additional mass transport induced by UV irradiation [82]."

- *The survey XPS spectrum is missing.*

The survey XPS spectra were added to Chapter 2.3.5 in the revised version: Figure 11, Figure 12, Figure 13.

- *How was the overlap between adjacent irradiated tracks (71%) in the case of aluminum alloy optimized?*

The overlap between adjacent irradiated tracks was chosen arbitrarily as it was defined through a given distance between adjacent tracks and recalculated into overlap afterwards.
This question was addressed in the revised version in Chapter 2.4.1, p. 95:
"To ensure that each point of treated areas was exposed to intensity values that are close to the peak of the Gaussian beam, a distance of 10 µm was chosen between scanning tracks, resulting in a 71% overlap between adjacent tracks."

- *Proof of MoS2 nanoribbons formation is needed. It is hard to learn from SEM images. "Nano" according to the IUPAC definition is limited by 100 nm.*

This question was addressed in the revised version in Chapter 3.4.2, p. 123:
"Here, the term nanoribbons is used due to the small thickness (less than 20 nm) of the obtained structures that have a ribbon-like shape. The width of these ribbons ranges from ~ 200 to ~ 115 nm. These ribbons are also tightly packed, being repeatedly induced with a ~ 422 nm period, which results in a high proportion of edge length to surface area. This in turn has a significant effect on the properties of the synthesized material, namely photoconductivity, which is demonstrated and discussed in detail below."
Additionally, Figures 26 and 28 were added to make the proof of nanoribbon formation more decisive.

- *The concentration of solution and thickness of the films (MoS2) are correlated. However, the concentration is rather low, at the level of mMs. Does the change in concentration at this level much affect the thickness? Are density changes relevant at such concentrations?*

Thank you for this inquiry; previously, the term “dense solution” was used in a confusing manner, meaning “concentrated solution”, though the difference in the literal density of the solution was neglectable. This is now corrected throughout the thesis.
Those questions were addressed in the revised version in Chapter 1.4.2, p. 58-59:
“The concentration of the liquid precursor solution directly affects the thickness of the precursor films obtained after drying the spin-coated solution on a hot plate. Due to the low concentration of the precursor compound, a variation of concentration from 0 to 48 mM does not affect the viscosity of the overall solution significantly. The film is spin-coated to thickness that depends primarily on the viscosity of the solution and to a lesser extent on the parameters on rotation speed during spin-coating [162,164]. During the subsequent drying step, the liquid organic solvents evaporate, leaving behind a thin solid film of the (NH4)2MoS4 precursor compound, the thickness of which is defined by (NH4)2MoS4’s concentration in the liquid solution.“

- *I would suggest clearly articulating the novelty of the results shown in Chapter 2.*

Changes were made throughout Chapters 1, 2 and Conclusion to better articulate the novelty and relevance of the results in question.

Prof. Nikolay Gippius

Thank you very much for the review; as far as I understand, no suggestions to modify the Thesis text are provided.

Prof. Toby Hallam

- *The chapter structure does not clearly contextualize the work in the thesis. The introduction should be rewritten into four chapters:*

Thank you for this suggestion.
Though it is in my opinion that including four separate chapters could make the thesis appear unbalanced, I have separated the Introduction Chapter in four subchapters in the manner that was proposed.

- *I note that some of the requested content is present in part in the existing chapter 1 and elsewhere throughout the thesis. The requested chapters should collect this content into the appropriate location in addition to writing new material.*

Throughout the revised version, the requested information was collected and placed to introductory subchapters, along with the additions made along the suggested guideline.

- *I ask that the results chapters be revised to present the work without self-referencing. Published work by the candidate should be mentioned in the same section as the individual attributions.*

I have removed self-referencing throughout the revised version.
It is worth noting that publication *#4: Averchenko AV, Salimon IA, Zharkova EV, Lipovskikh S, Somov P, Abbas OA, Lagoudakis PG, Mailis S. Laser-enabled localized synthesis of Mo1-xWxS2 alloys with tunable composition. Materials Today Advances. 2023 Jan;17:100351* was removed from list of publications on which the thesis is based after clearing out confusion about the Defense procedure. Some references were kept to this publication where relevant to mention matters outside the scope of the thesis.

- *I ask that the candidate extend the final chapter to include a more detailed discussion of the impact of the findings presented in the results chapters including a discussion of possible future work.*

A discussion of the impact of the findings and possible future prospects were added to the Conclusions section in the revised version.