

SPATIAL AND TEMPORAL SYMMETRY BREAKING IN NONLINEAR LASER LITHOGRAPHY

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Spatial and Temporal Symmetry Breaking in Nonlinear Laser Lithography

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We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

SPATIAL AND TEMPORAL SYMMETRY BREAKING IN NONLINEAR LASER LITHOGRAPHY

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Symmetry breaking is ubiquitous in nonlinear systems. This is also the case for Nonlinear Laser Lithography (NLL), in which an ultrafast laser beam incident on a material surface causes the infinite fold rotational symmetry of the material surface to be broken. In the case of linear polarization, line like structures are obtained that possess 2-fold rotational symmetry. We discuss two types of NLL, one due to the formation of oxide structures (Oxidation NLL) and the other due to material ablation (Ablation NLL). The existence of both types of structures is known for many years, however, although the regularity of oxidative structures has been significantly improved by our group earlier, the same was not true for ablative structures. Here, using the technique for Oxidation NLL and the parameters for ablative structures, we were able to achieve highly regular ablative structures which we call Ablation NLL. We demonstrate the coexistence of these two NLL structures on the same surface and how a plane can be tiled using them. Furthermore, we explore the phase space of NLL and determine the regions of the phase space occupied by the two NLL structures. We also demonstrate the versatility of NLL by obtaining Oxidation and Ablation NLL structures on several metals as well as on Silicon. We also discuss temporal symmetry breaking in NLL. If the laser beam is not incident normal to the surface and is tilted towards or away from the scanning direction, it can cause the period of the NLL structures to decrease or increase respectively. One can thus discern if a video of the beam creating a pattern while scanning over the surface along a line is run forward or backward. This dependence on the scanning direction leads to temporal symmetry breaking and is reminiscent of the Doppler effect. These symmetry breakings can be important for future research in this field along with possible commercial applications, some of which we have discussed here.

Keywords: Ultrafast Lasers, Nonlinear Laser Lithography, LIPSS, Doppler Effect, Self-organization, Symmetry Breaking, Material Processing, Nanostructures, Nanopatterning, Tiling, Conformity.



ÖZET

NONLINEAR LAZER LİTOGRAFİDE UZAMSAL VE ZAMANSAL SİMETRİ KIRILMASI

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Nonlinear sistemlerde simetri kırılması yaygındır. Bu durum Nonlinear Lazer Litografi (NLL) için de geçerlidir, ultrahızlı lazer ışının bir malzeme yüzeyi üzerine incidensi malzeme yüzeyinin sonsuz katı döngüsel simetrisinin kırılmasına neden olur. Doğrusal polarizasyon durumunda, 2-katı döngüsel simetriye sahip çizgisel yapılar elde edilir. Oksidasyon NLL'nin oluşumuna (Oksidasyon NLL) ve malzeme ablasyonuna (Ablasyon NLL) dayalı iki tür NLL'yi tartışıyoruz. Her iki yapı türünün varlığı yıllardır bilinmektedir, ancak daha önce grubumuz tarafından oksidasyon yapılarının düzenliliği önemli ölçüde iyileştirilmiş iken, aynı ablasyon yapıları için geçerli değildir. Burada, Oksidasyon NLL tekniği ve ablasyon yapıları parametreleri kullanarak, yüksek düzenli ablasyon yapıları elde ettik, bunları Ablasyon NLL olarak adlandırdık. Bu iki NLL yapısının aynı yüzeyde eş zamanlı olarak var olduğunu ve bunları nasıl döşeyebileceğimizi gösterdik. Ayrıca, NLL faz alanını keşfettik ve iki NLL yapısının işlediği faz alanı bölgelerini belirledik. Ayrıca, birçok metal ve silisyum üzerinde Oksidasyon ve Ablasyon NLL yapılarının elde edilebildiğini gösterdik. Ayrıca, NLL'de zaman simetri kırılmasını tartıştık. Lazer ışını yüzeye normal olmayan ve tarama yönüne doğru veya tarama yönünden uzak olmayan bir şekilde eğilirse, NLL yapılarının periyodunu azaltması veya artmasına neden olabilir. Bu şekilde, bir ışının video, bir çizgi boyunca yüzey üzerinde tarama yaparken bir desen oluştururken, ileriye doğru çalışıyor mu yoksa geriye doğru çalışıyor mu anlaşılabilir. Bu tarama yönüne bağımlılık, Doppler etkisi ile benzerdir ve bu simetri kırılmalarının gelecekteki bu alandaki araştırmalar ve bazı işletmeler için önemli olabileceği, burada tartışılan bazı uygulamalar da dahil olmak üzere, bu alandaki gelecekteki araştırmalar için önemlidir.

Anahtar sözcükler: Ultrahızlı Lazerler, Nonlinear Lazer Litografi, LIPSS,

Doppler Etkisi, Kendi Kendine Düzenleme, Simetri Kırılması, Malzeme İşleme, Nanoyapılar, Nanodizayn, Döşeme, Uygunluk.



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Contents

1	Introduction	1
2	Nonlinear Laser Lithography	4
2.1	Theory	4
2.2	Simulations	12
2.3	Experiments	15
3	Oxidation and Ablation NLL	17
3.1	Theory	17
3.1.1	Analysis	23
3.2	Simulations	26
3.3	Experiments	27
3.3.1	Setup	28
3.3.2	Ablation NLL in transmission mode	31
3.3.3	Coexistence on the same surface	33

3.3.4	Investigating the Phase Space	37
3.3.5	Tiling the plane	41
3.3.6	Versatility	46
3.3.7	Applications	50
4	The Doppler Effect	58
4.1	Theory	58
4.2	Simulations	67
5	Future prospects	75
5.1	A Third Type of NLL?	75
5.2	Period Shift	77
5.3	Vortex Beams with NLL	79
5.4	Conformity of NLL Structures	80
6	Conclusion	83

List of Figures

2.1	Numerical experiment showing NLL structures formed by vertically polarized laser beam.	12
2.2	Collision numerical experiment with initial scan performed with horizontal polarization while the second scan is performed with vertical polarization.	13
2.3	Collision numerical experiment with initial scan performed with vertical polarization while the second scan is performed with horizontal polarization.	14
2.4	Experiment showing NLL structures formed by vertically polarized laser beam on 60nm thick Titanium sample.	15
2.5	(Left)Collision experiment on 60nm thick Titanium sample with initial scan performed with vertical polarization while the second scan is performed with horizontal polarization (Right)Collision experiment on 60nm thick Titanium sample with initial scan performed with horizontal polarization while the second scan is performed with vertical polarization.	16

- 3.1 (i) The behavior of the fixed points with respect to the inverse logarithm of the number of pulses. A pitch-fork type bifurcation diagram emerges. Upon decreasing the PPS, we see that two new fixed points emerge. There are two stable ones corresponding to Oxidation and Ablation NLL structures while one is unstable. The green curve represents the height of Oxidation NLL structures while the blue curve represents the height of Ablation NLL structures. (ii) Change in total height with the inverse logarithm of the number of pulses. As the number of pulses is decreased, the total height decreases rapidly, reaches a minimum and then increases again. (iii) Heights of Oxidation and Ablation NLL structures presented separately. (iv) Plots showing the evolution of fixed points for the total height as the PPS is decreased. 25
- 3.2 Numerical experiment showing Oxidation and Ablation NLL on the same surface. The beam is scanned once at high PPS to obtain Oxidation NLL (yellow), the PPS is decreased for the second scan to obtain Ablation NLL structures (blue). 26
- 3.3 Numerical experiment showing Oxidation and Ablation NLL on the same surface. The beam is scanned once at high PPS to obtain Oxidation NLL (yellow), the PPS is decreased and the polarization is rotated by 90 degrees for the second scan to obtain Ablation NLL structures with the same orientation as the Oxidation NLL structures (blue). 27

3.4	Experimental setup for obtaining Oxidation and Ablation NLL on the same surface. A variable repetition rate Ultrafast fiber laser is used as the laser source, the beam is then collimated and guided towards the sample by various optical components. The beam is then focused onto the sample by a focusing objective. The sample rests on a 2d movable microscope stage, using which the sample can be moved to obtain NLL structures on a large area. Half wave plate and a polarizing beam splitter are used to provide intensity control. Another halfwave plate is used for polarization control. The resulting structures are imaged using an EMCCD camera connected to the microscope assembly.	29
3.5	First observation of Ablation NLL in transmission mode. The structures are obtained on 200nm thick Cobalt sample with a horizontally polarized laser beam. The average power reaching the surface is 0.2mW, the laser repetition rate is 2kHz and the beam scanning speed is 500 μ m/s. The structures are imaged using a 40x microscope objective.	32
3.6	One of the first observations of Oxidation and Ablation NLL on the same surface. The sample is a 110nm thick Cobalt sample. The bright squares contain Ablation NLL structures while the darker ones contain Oxidation NLL structures. Each square is 50 μ m $\times$ 50 μ m. The Oxidation NLL structures are obtained at a laser repetition rate of 1MHz, an average power of 6.8mW and scan speed of 20 μ m/s, while that for Ablation NLL structures are 2kHz, 0.067mW and 200 μ m/s respectively. The structures are imaged using a 40x microscope objective.	34
3.7	A zoomed-out version of Fig 3.5.	35
3.8	The structures of Fig 3.5 as seen under Stereo microscope with circular illumination.	36

- 3.9 (Left) SEM image of Oxidation and Ablation NLL structures on the same Cobalt surface formed side by side with the same laser polarization. (Right) cross-section images of Oxidation and Ablation NLL structures as seen under SEM. 37
- 3.10 A region of a grid of experiments performed to explore the phase space of the NLL structures. The scan speed is increased towards the right while power is increased going down. 38
- 3.11 Phase space of NLL structures based on pulse fluence and the number of pulses per spot. Ablation NLL structures occupy the top left region of the phase space while Oxidation NLL structures occupy the lower right region. The red crosses represent experiments that mark the boundaries of the NLL regions, the rest of the boundaries are our best guesses for where they should reside and how they might look like. 40
- 3.12 Oxidation NLL (red) and Ablation NLL (yellow) structures side by side, having the same orientation. The structures are observed using a Stereo microscope with circular illumination and imaged using a DSLR camera. 42
- 3.13 A Jigsaw puzzle type pattern created using Oxidation and Ablation NLL structures. The scanning stage is programmed to raster scan the desired pattern. Each square is $100\mu\text{m} \times 100\mu\text{m}$ in size, and created using the parameters described in Fig. 3.6. Oxidation NLL structures formed using vertical polarization are red in color while those formed using horizontal polarization are green. Ablation NLL structures formed using vertical polarization are brown in color while those formed using horizontal polarization are blue. . . 43

3.14	Transitions between Oxidation and Ablation NLL on Cobalt for horizontal and vertical polarization of the laser beam. a. Oxidation horizontal polarization to vertical polarization. b. Oxidation vertical polarization to horizontal polarization. c. Ablation vertical polarization to horizontal polarization. d. Ablation horizontal polarization to vertical polarization. e. Oxidation horizontal polarization to Ablation vertical polarization. f. Oxidation horizontal polarization to Ablation horizontal polarization. g. Oxidation vertical polarization to Ablation vertical polarization. h. Oxidation vertical polarization to Ablation horizontal polarization. i. Ablation vertical polarization to Oxidation horizontal polarization. j. Ablation vertical polarization to Oxidation vertical polarization. k. Ablation horizontal polarization to Oxidation horizontal polarization. l. Ablation horizontal polarization to Oxidation vertical polarization. Note: The experiments contain a 8 μ m-12 μ m overlap region while going from one process to the other.	45
3.15	Microscope images and their Fourier transforms of Oxidation and Ablation NLL structures formed using the parameters given in table 3.1. The images are taken using a 60x objective.	46
3.16	SEM images of Oxidation and Ablation NLL structures formed using the parameters given in table 3.1. The scale bar is 5 μ m. . .	48
3.17	Oxidation and Ablation NLL structures at optimal thicknesses as shown under a 100x microscope objective. Nb, Cr, Ti and Co, have film thickness of 60nm while that for Si, Al, and Ni are the same that the ones given in Table 3.1.	49
3.18	Oxidation NLL structures formed on Kopton tape, a heat resistant polymer. The structures are formed using the parameters mentioned in table 3.1.	51

3.19	Temperature sensor composed of Oxidation NLL structures on 110 thick Cobalt coated on Kapton tape. As the temperature changes, it causes the period of the structures to change which in turn changes the diffraction pattern and hence the color of the structures. This process can be used to measure temperature.	52
3.20	Red channel in each frame. We can see that the sample became redder when heated.	53
3.21	(Top) The hydrophilic Oxidation NLL structures formed on Si surface. (Bottom) The structures are then coated with 8nm of C_4F_8 , this makes the structures super hydrophobic.	55
3.22	The hydrophobicity of Oxidation NLL structures vs the thickness of the C_4F_8 coating.	56
3.23	(i) A Red-spotted Purple Admiral Butterfly (ii) Our rendition of the Admiral butterfly in the lab, created using Ablation NLL on 110nm Cobalt surface. The different colors are obtained by varying the polarization angle of the laser beam.	57
4.1	(a) Schematic showing the normal incidence of the laser beam on the sample. (b) Schematic showing the non-normal incidence of the laser beam with a tilt angle θ from the -z axis. (c) Surface intensity profile due to normally incident laser beam on a defect at the center. (d) (c) Surface intensity profile due to a tilted laser beam on a defect at the center.	59
4.2	Demonstrating Temporal Symmetry Breaking. (Left) The tilt angle is away from the scan direction giving rise to larger periods of the structures. (Right) The structure period is small when the beam is scanned in the direction of the tilt angle.	68

4.3	Behaviour of the structure period with changing tilt and observation angle.(Left)Plot of eq.4.34 considering tilt to be only along the x- direction. (Right)Plot of eq.4.34 considering tilt to be only along the y- direction.	69
4.4	Simulations showing the effect of x-tilt on the NLL structures with varying polarization angles.	70
4.5	Simulations showing the effect of y-tilt on the NLL structures with varying polarization angles.	71
4.6	Comparison of the periods of NLL structures predicted by eq. 4.34 with those obtained by numerical simulations.	72
4.7	Behaviour of the structure period with coupled x-y tilt at 45° polarization.	72
4.8	Simulations at 45° polarization with coupled x-y tilt. (Top) $\Phi_x = -20^\circ$ and $\Phi_y = -20^\circ$, (Center) $\Phi_x = 20^\circ$ and $\Phi_y = 20^\circ$, (Bottom) $\Phi_x = 20^\circ$ and $\Phi_y = -20^\circ$	73
4.9	Comparison of the periods of NLL structures predicted by eq. 4.34 with those obtained by numerical simulations. The plots are obtained by fixing the polarization to 45° and the x-tilt to a particular value and plotting the period vs the y-tilt.	74
5.1	Microscope image showing the edge of a region on Silicon surface scanned by a laser beam. The left region shows Oxidation NLL formed perpendicular to the polarization, the bright boundary shows Oxidation NLL structures parallel to the polarization and the dark region is unprocessed Silicon.	76
5.2	The third type of NLL (Oxidation NLL perpendicular to the laser polarization) as seen under SEM. The white arrow shows the laser polarization direction.	77

5.3	Period change observation in NLL on Silicon.	78
5.4	SEM image of the period change observation in NLL on Cobalt. .	79
5.5	(a) The standard fork grating to obtain vortex beams (b) The fork grating provided by Oxidation NLL.	80
5.6	Schematic showing a sketch of an experiment to study the confor- mity of NLL. The beam is raster scanned on the sample and a large area is covered with structures, the polarization is then suddenly changed to see whether the structures conform to the feedback from the older structures or not.	81

List of Tables

3.1	Parameters for obtaining Oxidaiton and Ablation NLL for various materials.	47
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Chapter 1

Introduction

Ultrafast lasers are lasers with extremely short pulses in the time domain. Due to their fast energy deposition property, they can cause processes that might not be possible with continuous wave lasers. From material ablation [1] to eye surgery [2, 3], ultra-fast lasers have found applications in various areas of research and daily life since their invention [4, 5]. One interesting phenomenon caused by the interaction of an ultrafast laser beam with a material sample is that of Laser-Induced Periodic Surface Structures (LIPSS). LIPSS were discovered in 1965 [6], they are ripple-like structures formed on the material surface. There are various types of LIPSS, some are formed parallel to the laser polarization [7] while others are perpendicular to the laser polarization [6, 8], some have large periods while others have shorter ones [9]. There is no known general model that provides an explanation for all types of LIPSS but there are models that try to explain each type of LIPSS individually. Initially observed LIPSS were perpendicular to the laser polarization, they were explained by the interaction of Surface Plasmon Polaritons (SPPs) with the incident Electric field [10, 11, 12]. The parallel structures were initially explained as being formed due to the interaction of the E-field with the scattered E-field [13]. Öktem et al. in 2013 introduced a type of parallel LIPSS formed by oxidation reactions [14]. The oxidation reactions occur at places of high intensity caused by the interference of the incident and scattered E-fields. They termed this oxidation LIPSS, Nonlinear

Laser Lithography (NLL). LIPSS are a great scientific mystery, some have even called them a scientific evergreen [15], however, they have not been widely adopted on a commercial level due to the problem of quality control [7, 16]. LIPSS are periodic but most approaches don't allow for covering large regions with coherent structures. The technique of NLL overcomes this problem and provides highly coherent periodic structures that can be used to cover a large area on a material surface. We will spend the second chapter of this thesis exploring the process of Nonlinear Laser Lithography as developed by Öktem et al. The theoretical, numerical, and experimental aspects of the NLL process are discussed.

As mentioned above, along with NLL, we have other types of LIPSS as well including those having structures perpendicular to the laser polarization. Applying the technique of NLL with the parameters for LIPSS perpendicular to the laser polarization, we were able to obtain highly ordered structures for the perpendicular LIPSS as well. And since it is explained via material ablation, we decided to call it Ablation NLL, while we call the NLL introduced by Öktem et al. as Oxidation NLL. We will use this nomenclature throughout this thesis. Although the presence of Oxidation and Ablation NLL has been known for a while, they have not been studied on the same surface before, to the best of our knowledge. The third chapter of the Thesis introduces a toy model that tries to capture the dynamics of the two NLL processes on the same surface. The insight from the toy model is used to run numerical experiments that show the coexistence of the two NLL processes. Experimental results are then discussed in detail, from the first observation of Ablation NLL to the coexistence of the two NLL processes on the same surface. A phase space analysis is performed to explore the parameter space of both processes. Furthermore, their versatility is also demonstrated by obtaining both types of structures on different metals and Silicon. The chapter ends with a discussion of some applications of NLL.

The above-mentioned chapter three deals with spatial symmetry breaking. The linearly polarized laser beam breaks the infinite fold symmetry of the sample surface and turns it into a 2-fold symmetry due to the line-like shape of both Oxidative and Ablative NLL structures. Chapter four deals with temporal symmetry breaking. Upon non-normal incidence of the laser beam on the sample

surface, the components of the incident E-field change due to the introduction of the z component of the wave vector. This in turn causes the surface intensity profile to change such that if the tilt is away from the scanning direction, the period of the structures increases while it decreases if the tilt is towards the scanning direction. This change in the period based on whether the beam is scanning forward or backward results in temporal symmetry breaking. An analytical model is developed to predict the periods of the NLL structures in the case of an arbitrary tilt angle. The predictions of the model are then tested against numerical simulations performed using a modified version of the theory of Oxidation NLL.

Chapter five discusses some future prospects for NLL research and finally, chapter six concludes the thesis.

Chapter 2

Nonlinear Laser Lithography

2.1 Theory

Nonlinear Laser Lithography (NLL) is a lithography technique that uses self-organization to form structures on a material surface. It has been demonstrated on various substances including metals and non-metals but our work mostly focused on NLL on metals so we will talk about structures on a metal surface.

The metal surface is not smooth, It contains mountains and valleys which can be several nano-meters in height and depth compared to the average height profile of the surface. When a laser pulse encounters such a metal surface, it scatters from the mountains. The scattering strength depends on the height of the mountains that scatter it. While the scattering is happening, the incident field is still present due to the finite time duration of the pulse. The two fields now present on the metal surface interfere with each other and form an interference pattern on the metal surface which gives an intensity pattern that is then felt by the metal surface. Within this intensity profile, there are regions where the energy delivered to the metal surface, exceeds the activation energy of the metal atoms. This causes the metal atoms to react with the environmental oxygen to form metal oxide. It is this metal oxide that is then seen as structures forming

on the surface of the metal.

Below, we provide a mathematical description of this entire process. The surface is modeled as a rough surface with a height profile given as $h(x, y) = \delta(x, y)\Delta h$ in the x-y plane. Where $\delta(x, y)$ is a random variable with an average value of 0 and a root mean squared (rms) value of 1 and Δh is the rms surface roughness. The incident beam is modeled as a pulse train composed of ultra-fast Gaussian pulses. The beam is incident on the surface along the z-axis where it encounters the surface at $z = 0$.

The incident Intensity is given as the sum of the intensities of the individual pulses.

$$I_{inc} = \sum_n I_n(x, y, t). \quad (2.1)$$

Each pulse is modeled as having a Gaussian profile in both spatial and temporal domains. The incident intensity due to each pulse is given as follows.

$$I_n(x, y, t) = I_0 \exp \left[-\frac{(x - x_{0,n})^2 + (y - y_{0,n})^2}{w^2} - \frac{(t - nT_R)^2}{\tau_p} \right], \quad (2.2)$$

where n is the pulse number, $(x_{0,n}, y_{0,n})$ are the coordinates where the center of the pulse is incident on the metal surface, w is the beam width, T_R is the round trip time of the laser cavity which determines the temporal separation between the pulses, and τ_p is the pulse duration.

To observe the interference that occurs on the metal surface, we need to discuss the behavior of the electric fields on the surface. To a good approximation, the time dependence can be ignored for pulses in the femtosecond regime. Consequently, we can assume the pulses to be rect functions in the time domain. Within the pulse duration, the incident electric field due to the n th pulse is given as follows.

$$\vec{E}_{inc_n}(x, y) = (E_x \hat{x} + E_y e^{i\phi} \hat{y}) e^{-\frac{(x - x_{0,n})^2 + (y - y_{0,n})^2}{2w^2}}, \quad (2.3)$$

where ϕ is the phase difference between the x and y components of the $\vec{E}$ field, allowing for arbitrary polarization.

The following analysis focuses on dynamics on the metal surface due to a single pulse, so we will drop the subscript n.

The $\vec{E}$ field will get scattered by the defects of the surface giving a scattered field profile on the surface. The scattered field is modeled as dipole radiation as follows.

$$\vec{E}_{scat}(\vec{r}) = \frac{\alpha k^2}{\varepsilon_0} \int_V \overleftrightarrow{G}(\vec{r}, \vec{r}') E_{inc}(\vec{r}') dV, \quad (2.4)$$

where $\vec{r} = r \cos\theta \hat{x} + r \sin\theta \hat{y}$ is the observation position, r' is the position of the scattering point, α is the polarizability, k is the wave vector and ε_0 is the permittivity of free space. $\overleftrightarrow{G}(\vec{r}, \vec{r}')$ is the dyadic Green's tensor which describes how an infinitesimal defect scatters the electric field. Next, we want to incorporate the effect of the surface height profile, we achieve this by converting the volume integral into a surface integral as follows.

$$\vec{E}_{scat}(\vec{r}) = \frac{\alpha k^2}{\varepsilon_0} \int_S \overleftrightarrow{G}(\vec{r}, \vec{r}') E_{inc}(\vec{r}') h(\vec{r}') dS, \quad (2.5)$$

where $h(\vec{r}')$ gives the surface height profile and the dyadic Green's Tensor is given as follows.

$$\overleftrightarrow{G}(\vec{r}, \vec{r}') = \left[\overleftrightarrow{I} + \frac{1}{k^2} \nabla^2 \right] G_0(\vec{r}, \vec{r}'), \quad (2.6)$$

where $\overleftrightarrow{I}$ is the identity matrix and $G_0(\vec{r}, \vec{r}') = \frac{e^{ik|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}$ is the scalar Green's function. Calculating the Laplacian we get the following components for the Green's tensor.

$$G_{xx} = \frac{1}{4\pi} \cos^2 \theta \frac{1}{r} + [3 \sin^2 \theta - 1] \left(\frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr}, \quad (2.7)$$

$$G_{xy} = \frac{1}{4\pi} \sin(\theta) \cos \theta \frac{1}{r} + 3 \sin \theta \cos \theta \left(\frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr}, \quad (2.8)$$

$$G_{yx} = \frac{1}{4\pi} \sin \theta \cos \theta \frac{1}{r} + 3 \sin \theta \cos \theta \left(\frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr}, \quad (2.9)$$

$$G_{yy} = \frac{1}{4\pi} \sin^2 \theta \frac{1}{r} + [3 \cos^2 \theta - 1] \left(\frac{1}{r^3} - \frac{ik}{r^2} \right) e^{ikr}. \quad (2.10)$$

The components of the scattered field can then be written as follows.

$$E(x, y)_x^x = \zeta \iint E_x(x', y') h(x', y') e^{ikr} \left[(3 \sin^2 \theta - 1) \left(\frac{1}{k^2 r^3} - \frac{i}{kr^2} \right) + \frac{\cos^2 \theta}{r} \right] dx' dy', \quad (2.11)$$

$$E(x, y)_x^y = \zeta \iint E_x(x', y') h(x', y') e^{ikr} \left[3 \sin \theta \cos \theta \left(\frac{1}{k^2 r^3} - \frac{i}{kr^2} \right) - \frac{\sin \theta \cos \theta}{r} \right] dx' dy', \quad (2.12)$$

$$E(x, y)_y^x = \zeta \iint E_y(x', y') h(x', y') e^{ikr} \left[3 \sin \theta \cos \theta \left(\frac{1}{k^2 r^3} - \frac{i}{kr^2} \right) - \frac{\sin \theta \cos \theta}{r} \right] dx' dy', \quad (2.13)$$

$$E(x, y)_y^y = \zeta \iint E_y(x', y') h(x', y') e^{ikr} \left[(3 \cos^2 \theta - 1) \left(\frac{1}{k^2 r^3} - \frac{i}{kr^2} \right) + \frac{\sin^2 \theta}{r} \right] dx' dy', \quad (2.14)$$

where $r = \sqrt{(x - x')^2 + (y - y')^2}$ and $\theta = \tan^{-1}(\frac{y-y'}{x-x'})$, $\zeta = \frac{\alpha k^2}{4\pi\epsilon_0}$ and $k = \frac{2\pi}{\lambda}$ with λ being the wavelength of the incident field. $E(x, y)_x^x$ gives the scattered electric field in the x direction due to the x component of the incident field, $E(x, y)_y^x$ gives the scattered electric field in the y direction due to the x component of the incident field, and so on. $E_x(x', y')$ and $E_y(x', y')$ are the x and y components respectively of the incident electric field at the point (x', y') . The above expressions give the total scattered electric field profile on the metal surface.

Rearranging the above expressions, we can write them in a more intuitive form, in terms of near and far fields, as follows.

$$E_x^{far}(x, y) = \zeta \iint h(x', y') [\cos^2 \theta E_x(x', y') - \sin \theta \cos \theta E_y(x', y')] \frac{e^{ikr}}{r} dx' dy', \quad (2.15)$$

$$E_y^{far}(x, y) = \zeta \iint h(x', y') [-\sin \theta \cos \theta E_x(x', y') + \dots \sin^2 \theta E_y(x', y')] \frac{e^{ikr}}{r} dx' dy', \quad (2.16)$$

$$E_x^{near}(x, y) = \zeta \iint \{h(x', y') [(3\cos^2 \theta - 1)E_x(x', y') + \dots 3 \sin \theta \cos \theta E_y(x', y')] (\frac{1}{k^2 r^3} - \frac{i}{kr^2}) e^{ikr}\} dx' dy', \quad (2.17)$$

$$E_y^{near}(x, y) = \zeta \iint \{h(x', y') [3 \sin \theta \cos \theta E_x(x', y') + \dots (3\sin^2 \theta - 1)E_y(x', y')] (\frac{1}{k^2 r^3} - \frac{i}{kr^2}) e^{ikr}\} dx' dy', \quad (2.18)$$

The scattered field along the x and y components is then given as:

$$E_{scat_x} = E_x^{near}(x, y) + E_x^{far}(x, y), \quad (2.19)$$

$$E_{scat_y} = E_y^{near}(x, y) + E_y^{far}(x, y), \quad (2.20)$$

The components of the total $\vec{E}$ field on the surface then become:

$$E_{surf_x}(x, y) = E_x + E_{scat_x}(x, y), \quad (2.21)$$

$$E_{surf_y}(x, y) = E_y + E_{scat_y}(x, y), \quad (2.22)$$

where $E_x = (\vec{E}_{inc})_x$ and $E_y = (\vec{E}_{inc})_y$.

Finally, we get the total $\vec{E}$ field on the surface as:

$$\vec{E}_{surf}(x, y) = E_{surf_x}(x, y)\hat{x} + E_{surf_y}(x, y)\hat{y}, \quad (2.23)$$

and the total intensity on the surface then becomes:

$$I_{surf}(x, y) = |\vec{E}_{surf}(x, y)|^2. \quad (2.24)$$

This surface intensity profile will contain regions of high and low intensity. For some regions, the energy deposited will surpass the activation energy of the metal atoms and they will react with the environmental oxygen to form metal oxide.

Now we will try to estimate the number of activated atoms on the metal surface. We will assume that all the power deposited by the laser pulses is absorbed by the metal. This assumption is justified for pulses in the sub-picosecond regime.

The differential activated volume due to a laser pulse is given as:

$$dV(x, y) = dA \int P(x, y, z) dz, \quad (2.25)$$

where $P(x, y, z)$ is the probability of activation and is dependent on the laser intensity. As discussed above, the metal atoms will only react with air if the deposited energy exceeds the activation energy for the reaction. This means that there is a minimum threshold intensity below which the reaction will not occur. Hence, we can write the probability function, $P(x, y, z)$ as follows:

$$P(x, y, z) = H(I_n(x, y, z) - I_{th}), \quad (2.26)$$

where H is the Heaviside function, $I_n(x, y, z)$ is the energy per second deposited by the n th pulse, and I_{th} is the threshold intensity. Here z also enters our analysis since the deposited intensity travels inside the metal as well causing oxidation to occur below the metal surface as well.

The intensity decays exponentially inside the metal surface.

$$I_n(x, y, z) = I_{surf_n}(x, y) e^{z/z_s}, \quad (2.27)$$

where z_s is the skin depth of the metal. There is a small probability of oxidation occurring below the threshold intensity as well, so we can replace the Heaviside function above with a Sigmoid function. The particular form of the sigmoid function is not important as long as we have tunable constants that allow us to change the derivative of the sigmoid at I_{th} . For demonstration purposes, we will take the logistic function as our sigmoid.

$$P(x, y, z) = S(I_n(x, y, z) - I_{th}), \quad (2.28)$$

$$S(I_n(x, y, z) - I_{th}) = \frac{1}{1 + e^{-k(I_n(x, y, z) - I_{th})}}. \quad (2.29)$$

Using the above expressions for I_n and $P(x, y, z)$, the differential activated volume element is then given by the following expression.

$$dV(x, y) = dA \int \frac{1}{1 + e^{-k(I_{surf_n}(x, y)e^{z/z_s} - I_{th})}} dz, \quad (2.30)$$

where k is a constant related to the reaction rate. The above integral is not trivial but, if we assume all the intensity to be absorbed by the time it reaches z_s , it can be evaluated numerically to get the activated depth.

The threshold intensity is given as follows:

$$I_{th} = \frac{\rho L z_s}{\tau_p}, \quad (2.31)$$

where ρ is the density of the metal, L is the effective heat capacity that includes the metal's specific heat, latent heat of fusion, and latent heat of evaporation, z_s is the skin depth, and τ_p is the pulse duration.

The number of metal atoms at each infinitesimal voxel $dV(x, y)$ of the metal surface that exceed their activation energy is given as follows.

$$N_M(x, y) = dV(x, y) \frac{\rho N_A}{M}, \quad (2.32)$$

where N_A is Avogadro's number and M is the molar mass of the metal.

From the above discussion we can see that as the incident intensity increases beyond the threshold intensity, we will get more and more activated atoms. The activation depth scales logarithmically with the incident intensity. Naively, this should mean that the amount of metal oxide (MO_x) produced should also increase logarithmically with intensity. But in practice, this does not happen. This is due to another limiting factor which is the amount of available oxygen.

The amount of available oxygen diminishes exponentially with the metal depth. Also, as the structures are formed, the depth beneath the metal surface at which oxygen is available decreases due to the accumulating metal oxide molecules which effectively increase the thickness of the sample. Thus the number of available oxygen molecules can be written as follows.

$$N_{O_2} = C_1 e^{-\frac{\eta h(x,y)}{h_c}}, \quad (2.33)$$

where C_1 and η are proportionality constants, $h(x,y)$ is the height of the MO_x structures, and h_c is the critical thickness parameter that incorporates the diffusion of O_2 in the metal.

At a particular incident intensity value, there are only so many metal atoms that can be activated. So, it is possible that ambient oxygen is available till a certain depth but the intensity gets lower than I_{th} before that depth. This will also cause the formation of MO_x to halt due to the lack of activated metal atoms. Thus we have two processes that limit the formation of NLL structures, the number of activated metal atoms and the available oxygen atoms. Stochiometrically, we will have the following scenario.

$$N_{MO_x} = \begin{cases} N_M & N_M < \beta N_{O_2} \\ \beta N_{O_2} & N_M > \beta N_{O_2} \end{cases}, \quad (2.34)$$

where β is a stoichiometric coefficient with a value depending on the amount of O_2 molecules required to form MO_x .

Finally, the increase in height of the sample surface due to the n th pulse, caused by the formation of the metal oxide structures, is given as follows.

$$\Delta h_n(x, y) = C_2 N_{MO_x}. \quad (2.35)$$

At the regions where the intensity due to I_{surf} exceeds I_{th} , each pulse causes a slight increase in height as shown above. After multiple pulses, the negative feedback provided by the limiting reagents limits the growth of the NLL structures and they saturate at a particular height value.

2.2 Simulations

A MATLAB script was written based on the above-mentioned theoretical model to simulate the formation of Oxidation NLL structures. The following figure shows a simple simulation of the laser beam scanning the surface with vertical polarization and giving rise to NLL structures.

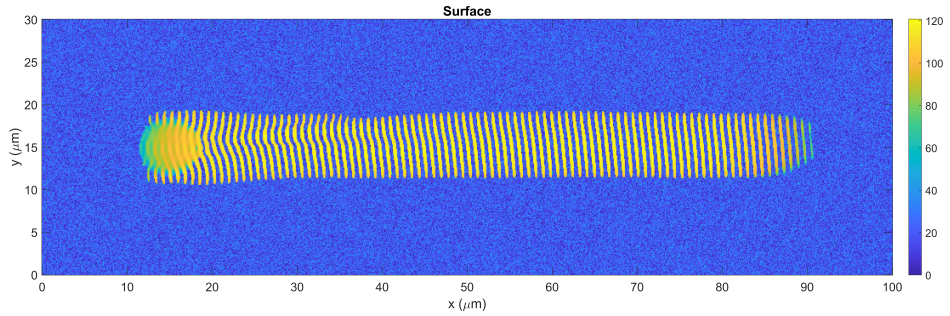


Figure 2.1: Numerical experiment showing NLL structures formed by vertically polarized laser beam.

As can be seen from the simulation in figure 2.1, the structures are slightly wavy in the beginning due to the feedback received by the large defect created by the laser burning the sample. However, the structures quickly heal themselves and align along the direction of polarization. It is this self-healing property of NLL that allows for the formation of highly coherent structures and allows for regular nano-patterning of large surfaces. This applies to other polarizations as well i.e. the structures align along the direction of polarization. In the case of circular polarization, we get a hexagonal pattern.

An interesting possibility that arises once we are able to simulate this process is of colliding two structures. This can be simulated by first generating one pattern and then scanning the laser beam again over the same pattern. Scanning with the same parameters again is trivial and does not have a significant effect on the structures, however, performing the second scan with different parameters can lead to interesting results. The following figures show two such collision numerical experiments that show an interesting result.

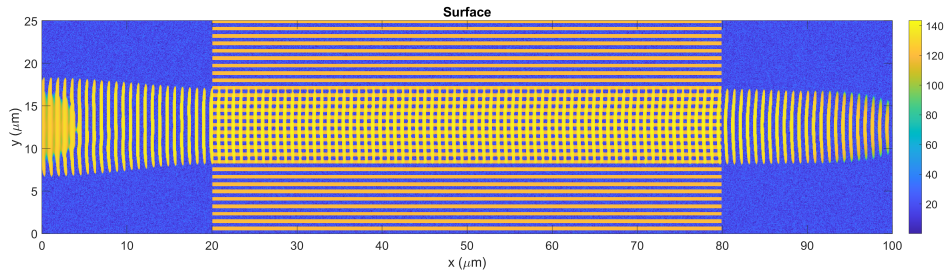


Figure 2.2: Collision numerical experiment with initial scan performed with horizontal polarization while the second scan is performed with vertical polarization.

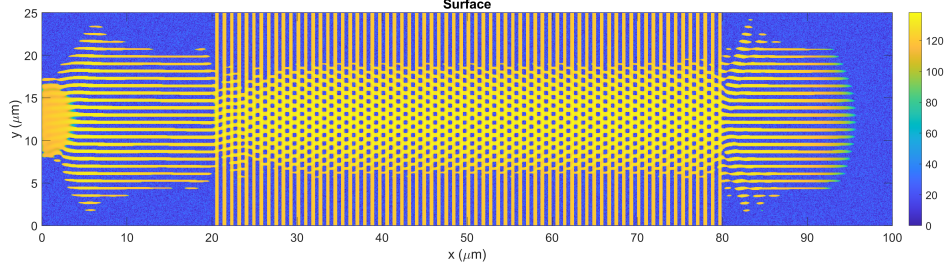


Figure 2.3: Collision numerical experiment with initial scan performed with vertical polarization while the second scan is performed with horizontal polarization.

In figure 2.2, the initial scan is performed with horizontal polarization and the second scan is performed with vertical polarization, while it is vice-versa in figure 2.3. Thus, we are essentially performing the same collision experiments in both with the only difference being the order of the scans. However, as clear from the figures, the resulting structures are two different lattices. In the first case, we get a square lattice, while we get a hexagonal lattice in the second case. This can be at least qualitatively explained by the fact that, though the experiments are similar, the feedback profiles in the two experiments are quite different. In the numerical experiment of figure 2.2, the feedback comes from straight lines that are on the order of the beam spot size in length, and thus the feedback to continue this linear arrangement is strong, added with the horizontal structures already existing, it will give us a square lattice. While in the other experiment, the feedback is provided by the points at the edges of the horizontal lines and is not strong enough to continue the linear arrangement causing the emergence of the hexagonal lattice which seems as the lower energy and thus preferred arrangement for the NLL system. Note that if the feedback is not strong enough, or if there are defects present, the structures can move towards a hexagonal arrangement in

the upper case as well.

2.3 Experiments

The above-mentioned simulation results can be realized quite nicely in experiments. The experimental setup used for the experiments is explained in the next chapter. The experiment below shows Oxidation NLL on 60nm thick Titanium metal coated on glass.

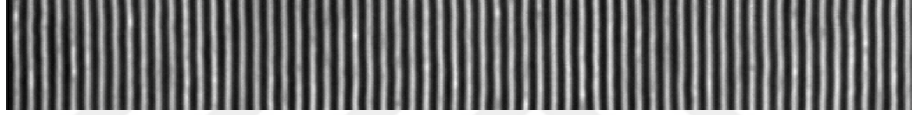


Figure 2.4: Experiment showing NLL structures formed by vertically polarized laser beam on 60nm thick Titanium sample.

Similarly, the collision numerical experiments shown above can also be realized experimentally on 60nm thick Titanium as shown below.

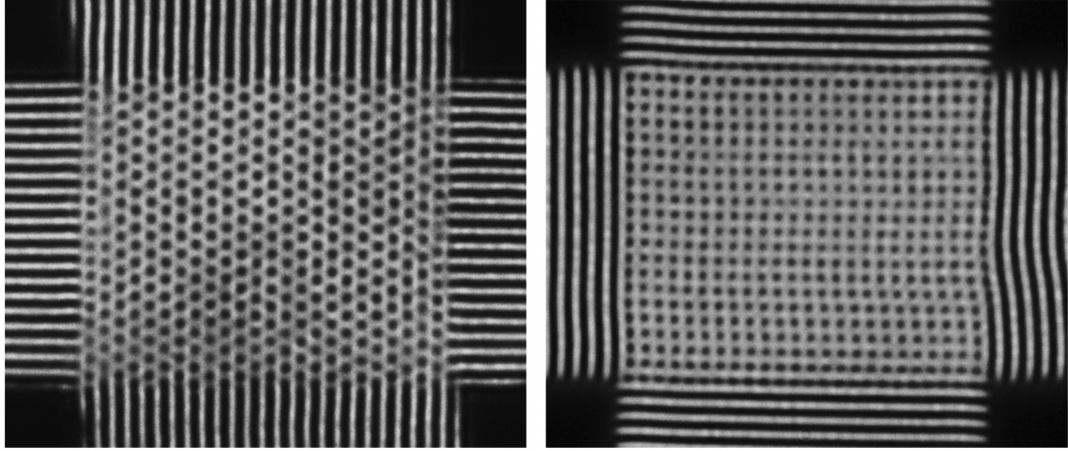


Figure 2.5: (Left) Collision experiment on 60nm thick Titanium sample with initial scan performed with vertical polarization while the second scan is performed with horizontal polarization (Right) Collision experiment on 60nm thick Titanium sample with initial scan performed with horizontal polarization while the second scan is performed with vertical polarization.

As evident, the match between theory and experiment is near perfect. Thus our theoretical model allows us to model the process of Oxidation NLL quite accurately. In the next chapter, we will build further on this understanding and incorporate another type of NLL due to Ablation into our model as well. This will allow us to observe the competition between the two different types of NLL on the same surface.

Chapter 3

Oxidation and Ablation NLL

3.1 Theory

The NLL process described in chapter 2 nicely explains the formation of metal oxide structures rising above the metal surface and being parallel to the laser polarization. But these are not the only structures that can come to reside on the sample surface. If the conditions change to a certain degree, a completely different specie can come to reside on the same surface as well. This other specie is composed of periodic structures dipping below the metal surface and formed perpendicular to the laser polarization due to material Ablation. We call this ablative specie, Ablation NLL, and the oxidative specie, Oxidation NLL.

These two species break the spatial symmetry of the sample surface. Initially, the surface is homogeneous in all directions and thus has an infinite-fold rotational symmetry. This rotational symmetry is broken when structures start forming on the sample surface. In case of linear polarization, we get linear structures that possess 2-fold rotational symmetry. The symmetry of the surface is also broken in the transverse direction, with Oxidation NLL structures rising above the surface and Ablation NLL structures dipping below it.

Both NLL processes use the same light field to trigger two perpendicular symmetry breakings. We will dive into the details of this process in this section. We will see that the two processes can share the spatial space on the metal surface but they occupy different regions in the parameter space of the incident laser beam. Firstly, let us discuss briefly how this second species is formed, and then we will observe the competition between the two species as they compete for space on the metal surface.

For the case of Ablation NLL, the structure formation occurs as follows. The incident light field excites surface electrons which also emit their own electromagnetic waves. This gives rise to surface waves called the surface plasmon polariton (SPP) modes of the metal surface. These SPP modes propagate perpendicular to the laser polarization at the air-metal interface. The interference between the Incident field and the SPP field then gives rise to an interference pattern. The regions of this interference pattern having constructive interference experience a higher intensity than the others, similar to the case of Oxidative NLL. But unlike the case of Oxidation NLL, the metal atoms are not oxidized, rather, they are ejected from the metal surface altogether. This causes the regions where Ablation occurs, to dip below the metal surface giving rise to structures that we call Ablation NLL. And since SPP waves travel perpendicular to the laser polarization, the Ablation NLL structures thus formed are perpendicular to the structures of Oxidation NLL.

The theoretical description of the whole process is quite complicated and is discussed in detail in the literature. Here, we will present a Toy Model that incorporates the above-mentioned effect of SPPs in the now-familiar theoretical model for Oxidation NLL. This Toy Model will not only help us to see the formation of Ablation NLL structures immediately but will also allow us to compare the two processes and observe their competition.

The Toy Model is described as follows. Assume that the $\vec{E}$ field is linearly polarized along the x-direction. From the discussions in chapter 2, we know that such a field will cause the formation of Oxidation NLL structures oriented along the x direction. Thus, to simplify the analysis we will consider the contribution

from only the G_{xx} component of Green's tensor and we will also ignore the angular (θ) dependence. The total $\vec{E}$ field on the surface can then be written as follows.

$$E_{surf} = E_0 + \zeta \iint \frac{E_0 h(x, y)}{|x - x'|} e^{ik_x |x - x'|} dx' dy'. \quad (3.1)$$

Now, if the conditions are right, the SPPs will also be excited on the metal surface, perpendicular to the laser polarization. SPPs decay exponentially with distance so we will also include an exponential decay factor to incorporate that. The total $\vec{E}$ field including the SPP contribution is given as follows.

$$E_{surf} = E_0 + \zeta \iint \frac{E_0 h(x, y)}{|x - x'|} e^{ik_x |x - x'|} + \kappa E_0 h(x, y) e^{-\beta |y - y'|} e^{ik_y |y - y'|} dx' dy', \quad (3.2)$$

where E_0 is the incident E-field, ζ is the scattering strength, k_x is the wave vector of the scattered field, $h(x, y)$ is the surface height profile, κ is the coupling coefficient between the incident field and the SPP modes, k_y is the SPP wave vector and $(2\beta)^{-1}$ is the SPP decay length.

Considering a smooth height profile with only a single defect at the center gives

$$h(x, y) = \delta(x, y) \Delta h, \quad (3.3)$$

putting this in (3.2) gives:

$$E_{surf}(x, y) = E_0 \left[1 + \zeta \Delta h \left(\frac{e^{ik_x |x|}}{|x|} + \kappa e^{-\beta |y|} e^{ik_y |y|} \right) \right]. \quad (3.4)$$

The intensity profile on the surface is given as,

$$I(x, y) = |E_{surf}(x, y)|^2. \quad (3.5)$$

This gives,

$$I(x, y) = E_0^2 \left[1 + 2\zeta \Delta h \left(\frac{\cos(k_x x)}{|x|} + \kappa e^{-\beta|y|} \cos(k_y y) \right) + \dots \right. \\ \left. + \zeta^2 \Delta h^2 \left(\frac{1}{x^2} + \kappa e^{-2\beta|y|} + \frac{2\kappa}{|x|} e^{-\beta|y|} \cos(k_x |x| - k_y |y|) \right) \right]. \quad (3.6)$$

Assuming Δh to be small, we can drop the last term containing Δh^2 from the above expression.

$$I(x, y) \approx E_0^2 \left[1 + 2\zeta \Delta h \left(\frac{\cos(k_x x)}{|x|} + \kappa e^{-\beta|y|} \cos(k_y y) \right) \right]. \quad (3.7)$$

The height of the oxidation structures scales exponentially with the increase in temperature as shown below. The change in height is also influenced by the available oxygen and the number of pulses incident on the sample per unit of time.

$$\Delta h = \eta(h) z_s f_R e^{\alpha T}, \quad (3.8)$$

where $\eta(h)$ gives the amount of available oxygen reactant as a function of height, z_s is the skin depth of the material, f_R is the repetition rate of the laser, α is the oxidation reaction rate coefficient and T is the temperature.

The temperature scales with the absorbed Fluence, as follows.

$$T = T_0 + \Delta T \frac{1}{\sqrt{1 + \frac{\tau_R}{\tau_0}}} = T_0 + \frac{F}{F_{ox}} \frac{1}{\sqrt{(1 + \frac{\tau_R}{\tau_0})}}, \quad (3.9)$$

where T_0 is the initial temperature, τ_R is the temporal distance between the pulses given by $\tau_R = f_R^{-1}$, τ_0 is the time taken for heat dissipation which depends on the thermal diffusivity of the sample, F is the laser fluence given by $F = I\tau_p$,

and $F_{ox} = I_{ox}\tau_p$ is the oxidation threshold fluence with I_{ox} being the oxidation threshold intensity. Thus, the above expression allows us to relate the change in height with intensity for structures formed by oxidation.

In the Ablation process the change in height, or the depth, scales logarithmically with the surface intensity as shown below.

$$\Delta h = z_s r_{ab} \ln\left(\frac{I}{I_{ab}}\right), \quad (3.10)$$

where r_{ab} is the ablation rate per pulse and I_{ab} is the threshold intensity for ablation.

Thus from (3.8) and (3.10) we get the following change in height due to both oxidation and ablation.

$$\Delta h = \eta(h) z_s f_R e^{\frac{I}{I_{ox}}(1+\frac{\tau_R}{\tau_0})^{-1/2}} - z_s r_{ab} \ln\left(\frac{I}{I_{ab}}\right), \quad (3.11)$$

where for simplicity we have absorbed e^{T_0} into $\eta(h)$ and α into I_{ox} . From the above expression, we can already see the competition dynamics between oxidation and ablation. Oxidation tries to raise the height of the surface while ablation tries to dig deeper below the surface. We will now try to explore this competition further by manipulating (3.11).

Taylor expanding the above expressions around I_{ab} , and truncating the series at 2nd order in intensity, I , gives:

$$\Delta h \simeq I^2 z_s \left(\frac{\eta(h) f_R A B^2}{2} + \frac{r_{ab}}{2 I_{ab}^2} \right) - I z_s \left(\eta(h) f_R B^2 I_{ab} - \eta(h) f_R B + \frac{2 r_{ab}}{I_{ab}} \right) + D, \quad (3.12)$$

where $A = e^{\frac{I_{ab}}{I_{ox}}(1+\tau_R/\tau_0)^{-1/2}}$, $B = (\sqrt{1 + \tau_R/\tau_0})/I_{ox}$, $C = B^2 I_{ab}^2/2 - B I_{ab} + 1$, and $D = z_s \eta f_R A C - 3 z_s r_{ab}/2$. $\eta(h)$ incorporates the saturation of the growth of the

structures. For now, we are interested only in the initial growth dynamics so we will take it as a constant, η , to simplify our analysis.

Now putting the form of the intensity given in (3.7) into the above equation gives,

$$\Delta h = \alpha(\Delta h)^2 \left[\frac{\cos(k_x x)}{|x|} + \kappa e^{-\beta|y|} \cos(k_y y) \right]^2 + \beta \Delta h \left[\frac{\cos(k_x x)}{|x|} + \kappa e^{-\beta|y|} \cos(k_y y) \right] + \gamma, \quad (3.13)$$

where

$$\alpha = 4I_0^2 \zeta^2 z_s \left[\frac{\eta f_R A B^2}{2} + \frac{r_{ab}}{2I_{ab}^2} \right],$$

$$\beta = 4I_0^2 \zeta z_s \left[\frac{\eta f_R A B^2}{2} + \frac{r_{ab}}{2I_{ab}^2} \right] - 2I_0 \zeta z_s \left[\eta f_R B^2 I_{ab} - \eta f_R B + \frac{2r_{ab}}{I_{ab}} \right],$$

and

$$\gamma = I_0^2 z_s \left[\frac{\eta f_R A B^2}{2} + \frac{r_{ab}}{2I_{ab}^2} \right] - I_0 z_s \left[\eta f_R B^2 I_{ab} - \eta f_R B + \frac{2r_{ab}}{I_{ab}} \right] + D.$$

Considering the change in height due to each pulse, we can write a continuous version of (3.13) with time step Δt taken as the temporal pulse to pulse separation, τ_R . This gives us the following continuous nonlinear differential equation for the height of the NLL structures.

$$\frac{\partial h}{\partial t} \simeq \alpha h^2 \left[\frac{\cos(k_x x)}{|x|} + \kappa e^{-\beta|y|} \cos(k_y y) \right]^2 + \beta h \left[\frac{\cos(k_x x)}{|x|} + \kappa e^{-\beta|y|} \cos(k_y y) \right] + \gamma. \quad (3.14)$$

As argued earlier, the above equation can also be seen as the two oxidation and ablation species competing with each other. To see it more clearly, we can separate the height contribution due to the parallel oxidation structures and the perpendicular ablation structures as follows.

$$h = h_{\parallel} - h_{\perp}. \quad (3.15)$$

This gives,

$$\begin{aligned} \partial_t h_{\parallel} \simeq & \alpha h_{\parallel}^2 [\cos(k_x x)/|x|]^2 + \beta h_{\parallel} \cos(k_x x)/|x| \dots \\ & - \alpha h_{\parallel} h_{\perp} \kappa e^{-\beta|y|} \cos(k_y y) \cos(k_x x)/|x| + \gamma_1 \end{aligned} \quad (3.16)$$

$$\begin{aligned} \partial_t h_{\perp} \simeq & \alpha h_{\perp}^2 [\kappa e^{-\beta|y|} \cos(k_y y)]^2 + \beta h_{\perp} \kappa e^{-\beta|y|} \cos(k_y y) \dots \\ & + \alpha h_{\parallel} h_{\perp} \kappa e^{-\beta|y|} \cos(k_y y) \cos(k_x x)/|x| - \gamma_2 \end{aligned} \quad (3.17)$$

where $h_{\parallel}$ corresponds to the height of oxidation NLL structures while $h_{\perp}$ to that of ablation NLL structures, and γ_1 and γ_2 are such that, $\gamma_1 + \gamma_2 = \gamma$ with γ defined above.

To simplify the above equations further, we apply coarse-graining. We ignore the modulation in space and observe what happens to the $h_{\parallel}$ and $h_{\perp}$ on a single point. This strips the above equations off of the variable coefficients and leaves us with just the height variables as follows.

$$\partial_t h_{\parallel} \simeq \alpha h_{\parallel}^2 + \beta h_{\parallel} - \alpha h_{\parallel} h_{\perp} + \gamma_1, \quad (3.18)$$

$$\partial_t h_{\perp} \simeq \alpha h_{\perp}^2 + \beta h_{\perp} + \alpha h_{\parallel} h_{\perp} - \gamma_2. \quad (3.19)$$

The above equations are in a typical form of the nonlinear dynamical equations for the populations of competing species and we can analyze them to observe the competition dynamics between the growth of oxidation and ablation NLL structures.

3.1.1 Analysis

We can analyze the above equations better by performing dynamical analysis on the above equations. Coarse graining the above equations and combining the heights of the Oxidation and Ablation NLL structures, we get the following simpler nonlinear differential equation.

$$\partial_t h \simeq \alpha h^2 + \beta h + \gamma. \quad (3.20)$$

This equation has the following fixed points:

$$h_{1,2}^* = \frac{-\beta \pm \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha}. \quad (3.21)$$

These fixed points depend on the number of laser pulses incident per spot on the sample (PPS). At high pulse numbers, we have only one fixed point. We can only obtain Oxidation NLL with large PPS. When the number of pulses is decreased, we get another fixed point. Thus Ablation NLL becomes possible when the number of pulses per spot is low. This is pictorially represented in the figure below.

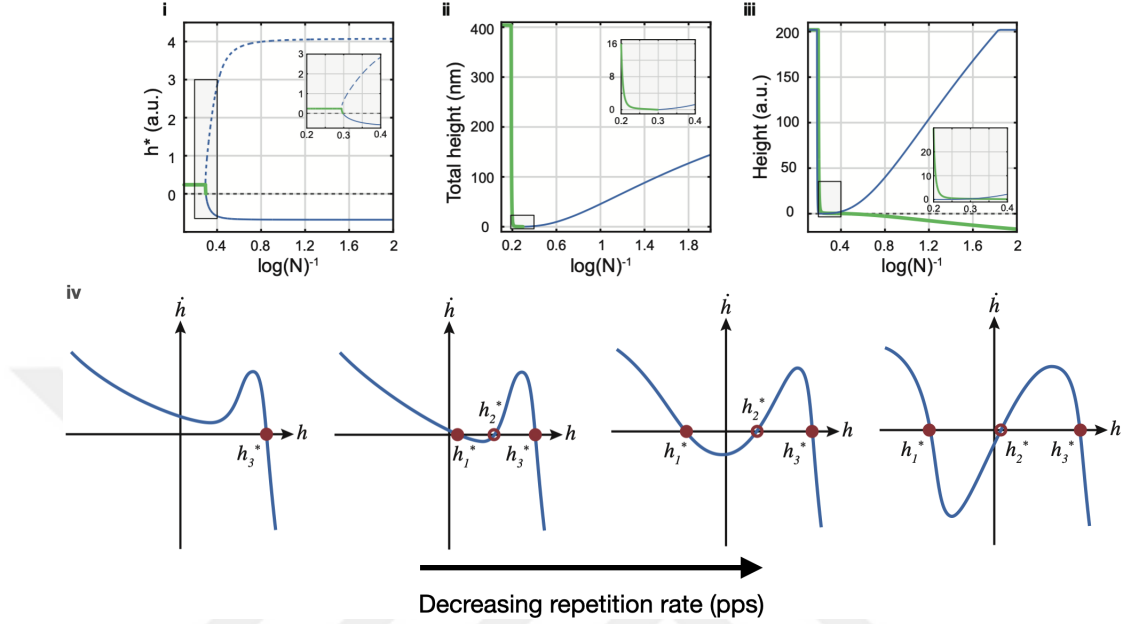


Figure 3.1: (i) The behavior of the fixed points with respect to the inverse logarithm of the number of pulses. A pitch-fork type bifurcation diagram emerges. Upon decreasing the PPS, we see that two new fixed points emerge. There are two stable ones corresponding to Oxidation and Ablation NLL structures while one is unstable. The green curve represents the height of Oxidation NLL structures while the blue curve represents the height of Ablation NLL structures. (ii) Change in total height with the inverse logarithm of the number of pulses. As the number of pulses is decreased, the total height decreases rapidly, reaches a minimum and then increases again. (iii) Heights of Oxidation and Ablation NLL structures presented separately. (iv) Plots showing the evolution of fixed points for the total height as the PPS is decreased.

As evident from figure 3.1, we get a bifurcation diagram with the critical parameter being the number of pulses per spot. We get a pitch-fork type bifurcation that allows the system to move from Oxidation NLL to Ablation NLL upon reducing the number of pulses incident per spot.

3.2 Simulations

Using the above model, we can not only simulate oxidation NLL as in Chapter 2 but we can also incorporate the effect of SPP's to get Ablation NLL. As shown in the previous section, the repetition rate that determines the pulses per spot (PPS) is one of the important parameters that allows us to move from Oxidation NLL to Ablation NLL and vice-versa. Increasing the repetition rate allows us to obtain Oxidation NLL while we get Ablation NLL upon reducing the repetition rate. Thus we can obtain Oxidation and Ablation NLL on the same surface by controlling the repetition rate. The simulations using the above theoretical model are shown below.

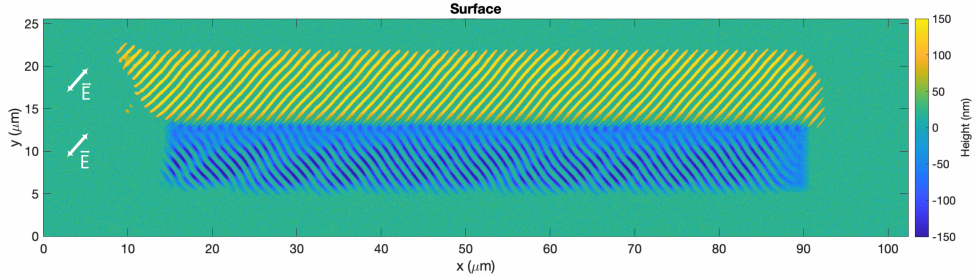


Figure 3.2: Numerical experiment showing Oxidation and Ablation NLL on the same surface. The beam is scanned once at high PPS to obtain Oxidation NLL (yellow), the PPS is decreased for the second scan to obtain Ablation NLL structures (blue).

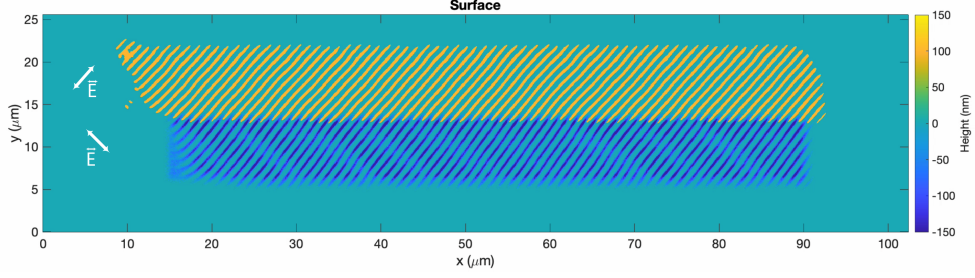


Figure 3.3: Numerical experiment showing Oxidation and Ablation NLL on the same surface. The beam is scanned once at high PPS to obtain Oxidation NLL (yellow), the PPS is decreased and the polarization is rotated by 90 degrees for the second scan to obtain Ablation NLL structures with the same orientation as the Oxidation NLL structures (blue).

In both simulations, initially, the laser is scanned with a high repetition rate (1MHz) with 45° polarization to get Oxidation NLL (yellow region), the repetition rate is then decreased to get Ablation NLL (blue region). In the upper simulation, the polarization is kept the same for both scans while it is rotated by 90° for the second scan in the lower figure. Thus we see that uniform surface symmetry is broken in opposite directions by the two NLL processes, Oxidation NLL structures rise above the surface while Ablation NLL structures dive below it. We also see that the Oxidation NLL structures are aligned parallel to the polarization, while Ablation NLL structures align perpendicular to the laser polarization.

3.3 Experiments

Oxidation and Ablation NLL are well known at this point in time and both have well-established theoretical and experimental foundations. However, in the literature, they are presented as two separate entities that have nothing to do with each other. Naturally, this makes one wonder that if they are both LIPPS then how come they are both never studied together? We set out to do exactly that. This investigation gave rise to further questions. Can we have them exist together on the same surface? What are the environments in which we get one

or the other structures and most importantly, can we identify a small set of parameters, changing which will allow us to transition from one type of NLL to another? This section provides the answers to these questions.

3.3.1 Setup

The environments in which oxidation and ablation NLL form are well known in the literature. Öktem et al. used a femtosecond pulsed laser to obtain Oxidation NLL on a thin (60nm) Titanium sample. Similarly, Ablation NLL was obtained by many groups using high-energy pulses on bulk samples. To study them together, one had to devise an experiment that allowed these environments to coexist or at least that allowed a smooth transition from one environment to another.

To have higher control over the laser parameters, we used a commercial laser capable of outputting pulses at different repetition rates and pulse energies. The polarization and average intensity were controlled using free-space optics embedded in the setup. The schematic of the setup is shown below [14].

The other step in providing coexisting environments favorable for both oxidation and ablation NLL was to use a sample that allows for the growth of both structures. In the literature, there are no strict sample requirements for achieving either type of NLL. They are supposed to form on any metal surface. Experimentally, however, working with bulk samples has some challenges. For instance, it is not easy to polish them well enough such that the surface defects do not play a significant role in distorting the structures. Focusing light on the sample is also problematic since the formation of ablation plasma at high intensity needs to be observed to know whether the laser is focused on the sample or not; and even if it is observed, it is hard to know the exact position of the focus in the vertical direction, the surface can be anywhere within the Rayleigh range of the beam. This problem gets aggravated in the case of oxidation NLL, which requires lower intensity. So, if the surface is within the Rayleigh range but not at the focus, it will show plasma at high enough intensity but it might not allow for the growth of oxidation NLL structures when the intensity is lowered to levels required for

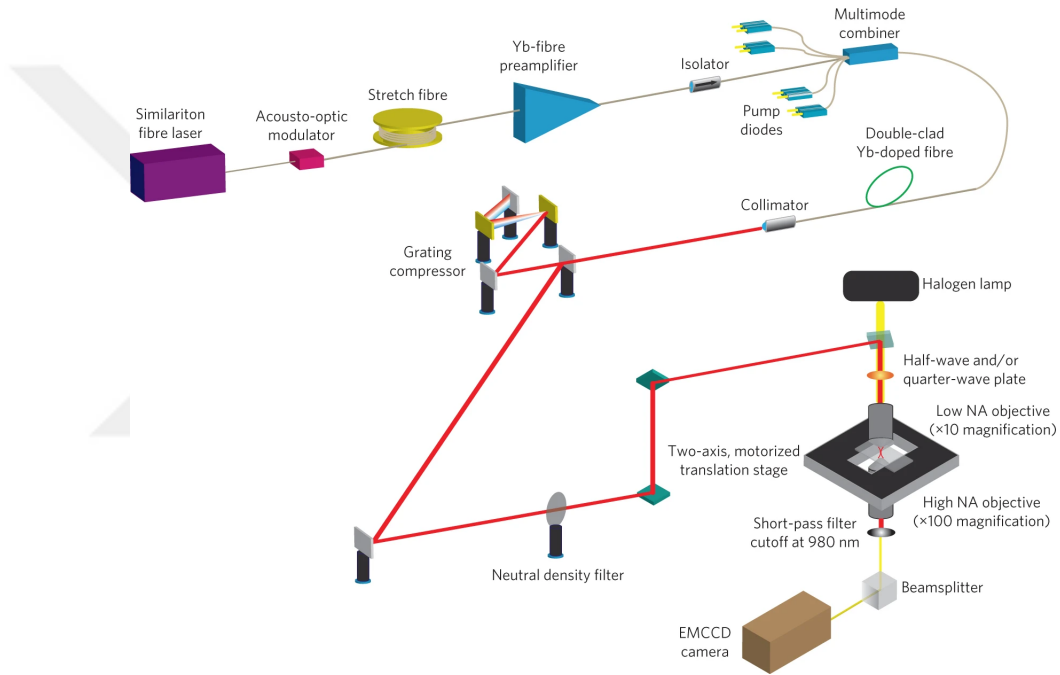


Figure 3.4: Experimental setup for obtaining Oxidation and Ablation NLL on the same surface. A variable repetition rate Ultrafast fiber laser is used as the laser source, the beam is then collimated and guided towards the sample by various optical components. The beam is then focused onto the sample by a focusing objective. The sample rests on a 2d movable microscope stage, using which the sample can be moved to obtain NLL structures on a large area. Half wave plate and a polarizing beam splitter are used to provide intensity control. Another halfwave plate is used for polarization control. The resulting structures are imaged using an EMCCD camera connected to the microscope assembly.

their formation. Also if the metal surface has a thickness gradient then the beam will become out of focus as the beam is scanned for structure formation. Thus forming structures on bulk samples is quite challenging. Furthermore, once the structures are formed, they need to be imaged using a Scanning Electron Microscope (SEM) or similar equipment, which can be significantly time-consuming. One workaround for the imaging problem is to use a movable stage coupled to a microscope that allows for imaging using light reflected from the sample. This will allow for dynamic imaging of the sample and might also help in plasma detection to improve focusing. This method works satisfactorily for well-polished samples with uniform thickness. Especially for observing the formation of oxidation NLL, it is a viable option. However, for ablation NLL, since the surface is being modified by only 10s of nanometers, there isn't enough contrast between the modified and unmodified parts of the sample and thus the structures are hard to resolve. Furthermore, if a sample is very shiny or if the absorption coefficient of the metal oxide is similar to that of the metal for the wavelength of the illumination light, then even the oxidation NLL structures are hard to resolve and this method fails but that is not the case for most metals. Note that the illumination light sources mentioned here are incoherent, the results might differ if a coherent light source is used for imaging.

From the above arguments, it is clear that using bulk samples for obtaining Oxidation and Ablation NLL is not a very viable option, nor is imaging them using reflected light. Note that we not only want a sample that allows for the formation of both Oxidation and Ablation NLL structures, but we also want an imaging setup that allows us to observe both of these structures together; so that we can analyze them together and preferably dynamically. For these reasons, the technique used by Öktem et al., of using a sample thin enough that it allows for the formation of oxidation NLL structures and also allows for the possibility of imaging using transmitted light, seemed like a favorable choice. In their technique, they coat a thin layer of metal ($\sim 60\text{nm}$) on a glass slide. The coating procedure ensures the deposition of a uniformly thick layer of the metal on the glass sample with low rms surface roughness. Once coated, this sample is then placed on a moveable stage coupled to a microscope and laser setup that

allows for structure formation, and imaging using light transmitted through the sample. Using a camera also connected to the setup, the surface is brought into focus. The laser light is then focused onto the surface using the camera along with a translation stage that can move the focusing objective toward or away from the sample. Since the sample is thin, there is good contrast between the surface and the oxidation NLL structures, which allows for better imaging. This process thus eliminates the problems mentioned above for bulk samples and imaging using reflected light by allowing the formation of good-quality oxidation NLL structures along with providing a very efficient imaging setup for high-resolution imaging.

3.3.2 Ablation NLL in transmission mode

Because of the superiority of the approach used by Öktem et al., and the possibility that their method might allow for a similar control for Ablation NLL as well as it did for Oxidation NLL, we decided to use this approach. However, the challenge here was the ablation process itself. Although oxidation can occur with thin samples that allow for good transmittance, ablation was never tried with thin samples before. Initial trials with 50 nm thick Cobalt sample showed that while Oxidation NLL can easily be observed at this thickness as expected, it is too thin for obtaining Ablation NLL structures. At high pulse energies required for ablation, the part of the sample illuminated by the laser pulses ablates as a whole without leaving any structures. Knowing that we can achieve ablation for bulk samples, there was a possibility of obtaining Ablation NLL structures with samples thick enough that the metal doesn't get ablated as a whole while thin enough that it allows imaging using transmitted light. The problem was thus reduced to a thickness optimization problem. After trying different thickness values, the first Ablation NLL in the transmission mode was observed in 200nm thick Cobalt sample, shown below.

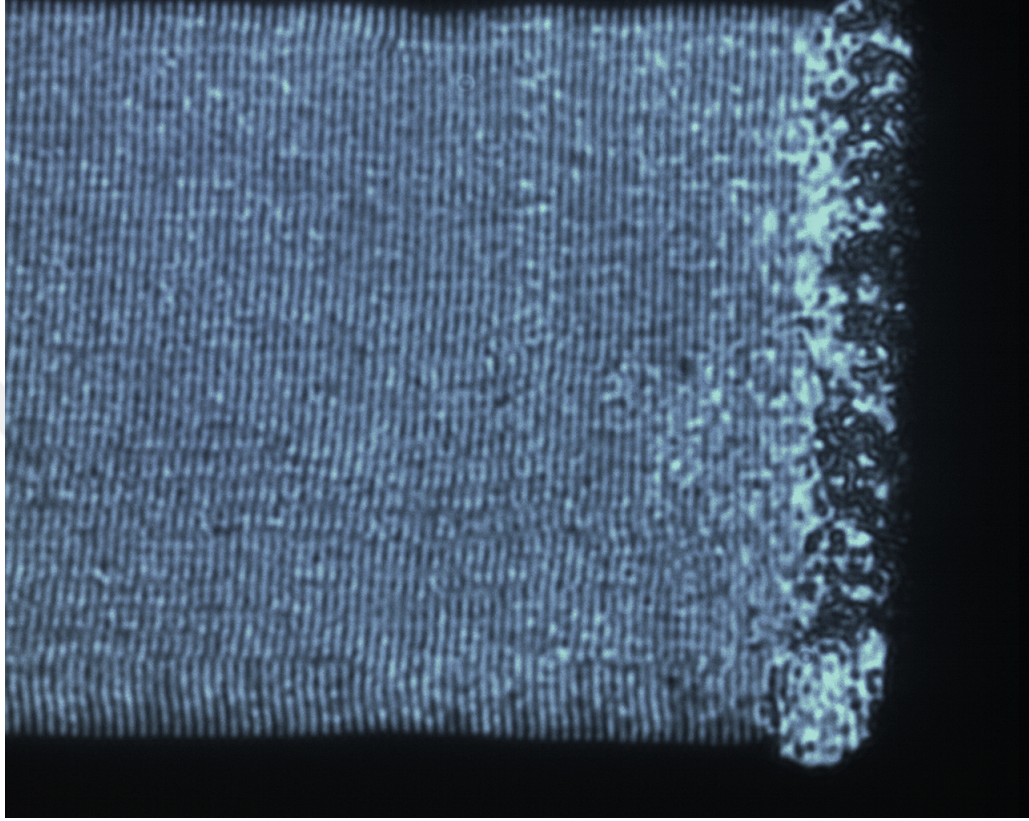


Figure 3.5: First observation of Ablation NLL in transmission mode. The structures are obtained on 200nm thick Cobalt sample with a horizontally polarized laser beam. The average power reaching the surface is 0.2mW, the laser repetition rate is 2kHz and the beam scanning speed is 500 μ m/s. The structures are imaged using a 40x microscope objective.

The bright regions in figure 3.5 are the surface of the glass slide, while darker regions are Cobalt metal. These structures are formed by scanning the horizontally polarized beam on the Cobalt surface at a speed of 500 μ m/s at a pulse repetition rate of 2KHz. The region on the right edge is the area where the laser stops to change direction; the increased time spent there causes too many high-energy pulses to be incident on the same spot, destroying the structures.

3.3.3 Coexistence on the same surface

The next challenge was to obtain both Oxidation and Ablation NLL structures on the same surface. Oxidation NLL structures can only reach a certain depth due to the negative feedback mechanisms mentioned in chapter 2, so to observe them in transmission mode a thin sample was necessary. In a thick sample, they might not reach a depth deep enough that light can penetrate the remaining metal layer and reach the camera. While the Ablation NLL structures required a sample thick enough that the high energy pulses do not ablate the metal surface as a whole. Luckily, the structures met each other halfway and both Oxidation and Ablation NLL structures were obtained on the same Cobalt sample with a thickness of 110nm. The figures below show one of the first results showing the coexistence of Oxidation and Ablation NLL structures on the same Cobalt sample having a thickness of 110nm.

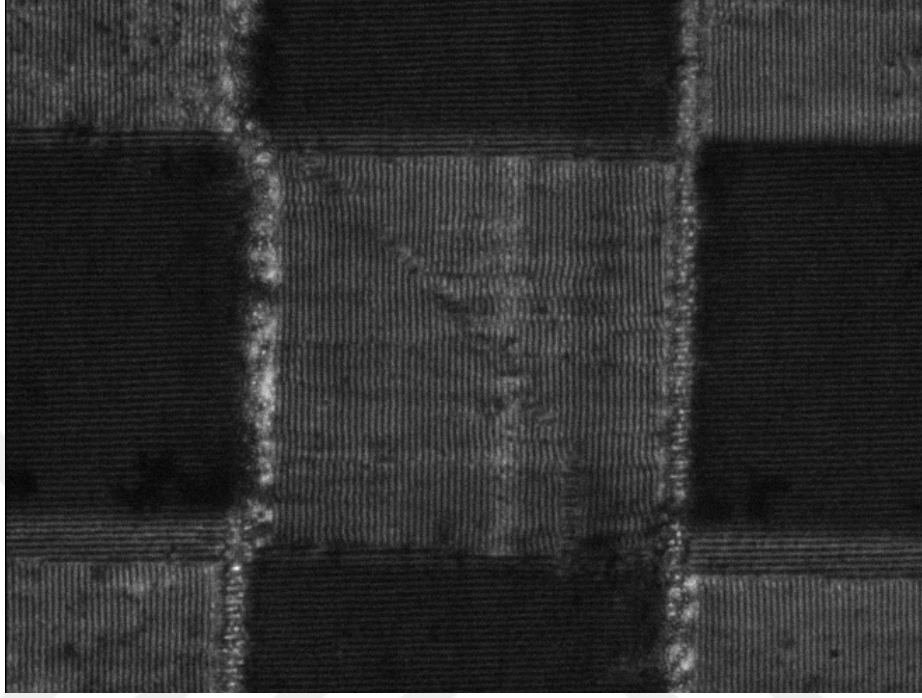


Figure 3.6: One of the first observations of Oxidation and Ablation NLL on the same surface. The sample is a 110nm thick Cobalt sample. The bright squares contain Ablation NLL structures while the darker ones contain Oxidation NLL structures. Each square is $50\mu\text{m} \times 50\mu\text{m}$. The Oxidation NLL structures are obtained at a laser repetition rate of 1MHz, an average power of 6.8mW and scan speed of $20\mu\text{m/s}$, while that for Ablation NLL structures are 2kHz, 0.067mW and $200\mu\text{m/s}$ respectively. The structures are imaged using a 40x microscope objective.

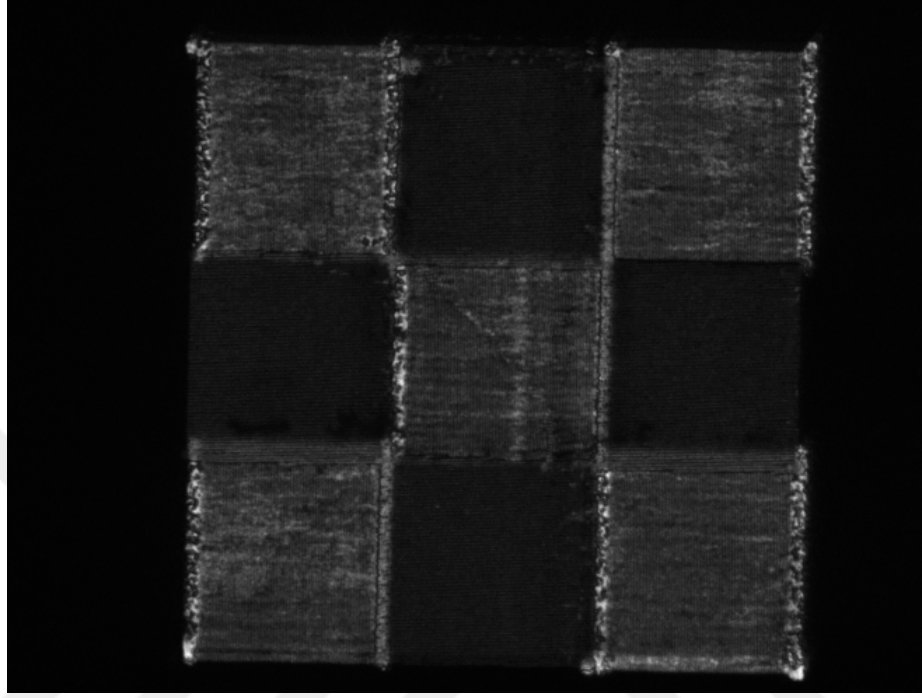


Figure 3.7: A zoomed-out version of Fig 3.5.

The bright regions in figures 3.6 and 3.7 are composed of Ablation NLL structures while the darker regions are Oxidation NLL structures made of Cobalt oxide. The totally black surrounding region is Cobalt metal. The laser beam used to obtain them was horizontally polarized. As can be seen from the figure, the oxide structures are aligned parallel to the polarization while ablation structures are formed perpendicular to it. The grid shape was chosen to demonstrate control over the two processes of NLL structure formation. To observe the diffraction properties of the pattern, we placed it under a stereo microscope having circular illumination. The resulting color pattern observed under the stereo microscope is shown below. The image is taken using a mobile phone camera attached to the microscope.

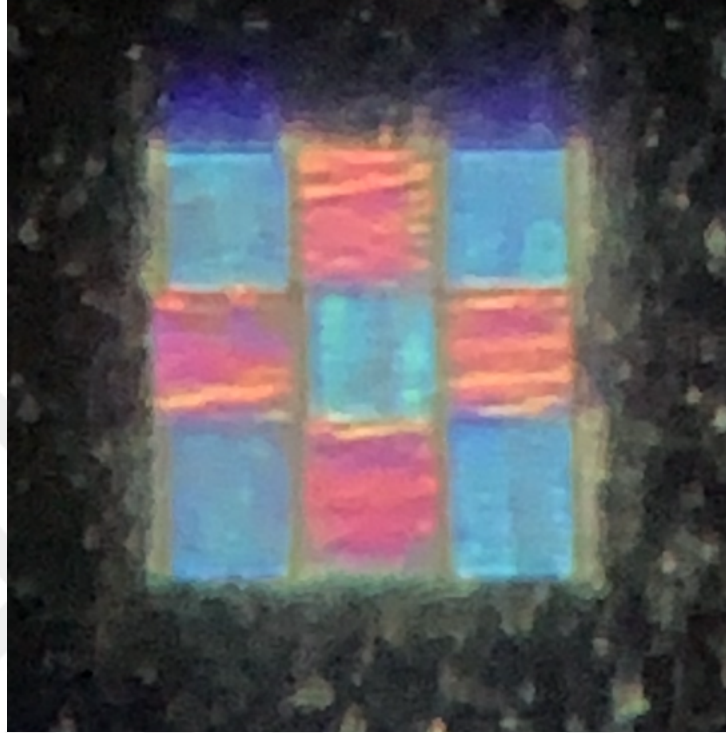


Figure 3.8: The structures of Fig 3.5 as seen under Stereo microscope with circular illumination.

We then observed the two structures side by side under SEM to get a better idea of the surface modulations involved in the two processes on the Cobalt surface. The SEM images are shown below.

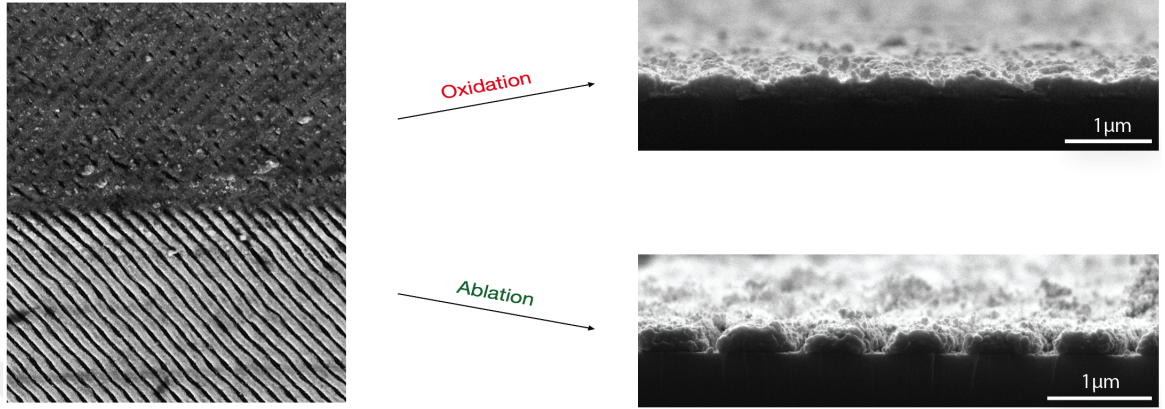


Figure 3.9: (Left) SEM image of Oxidation and Ablation NLL structures on the same Cobalt surface formed side by side with the same laser polarization. (Right) cross-section images of Oxidation and Ablation NLL structures as seen under SEM.

In Fig. 3.9, the left sub-figure shows the top view of the structures formed such that they are oriented $\pm 45^\circ$ from the line joining them. The top right sub-figure shows the cross-section taken from the Oxidation NLL section while the bottom right subfigure shows the cross-section of the Ablation NLL structures. As clearly visible, the modulation for the Oxidation NLL structures is above the surface of the metal while the metal has been removed from the regions between the Ablation NLL structures, exposing the surface of the glass slide below.

3.3.4 Investigating the Phase Space

After obtaining both types of NLL structures on the same surface, we wanted to further explore the formation environments of these NLL structures. From the literature, it was clear that Ablation NLL requires a low number of pulses per spot but high pulse energies while Oxidation NLL requires a large number of pulses per spot having low pulse energies. The oxidation process requires the cumulative effect of many pulses while ablation can occur with just a few pulses incident on each spot. It was based on this understanding that we were able to obtain the NLL structures shown above. But what are the boundaries of these

processes in the phase space? What is the lowest number of pulses that will allow us to obtain Oxidation NLL, what is the minimum fluence required, and similarly, what are the limits for the Ablation NLL process? These questions have not been explored in the literature to our knowledge. To answer these questions we decided to explore the phase space of the NLL processes, spanned by the parameters, Pulse Fluence (F), and the number of pulses per spot (N).

To explore the phase space we performed multiple experiments at different points in the phase space. The movable stage was programmed to perform multiple experiments in the form of a grid with the speed increasing along the x direction, while the average laser power increasing along the $-y$ direction. The grid of experiments once completed looked like follows.

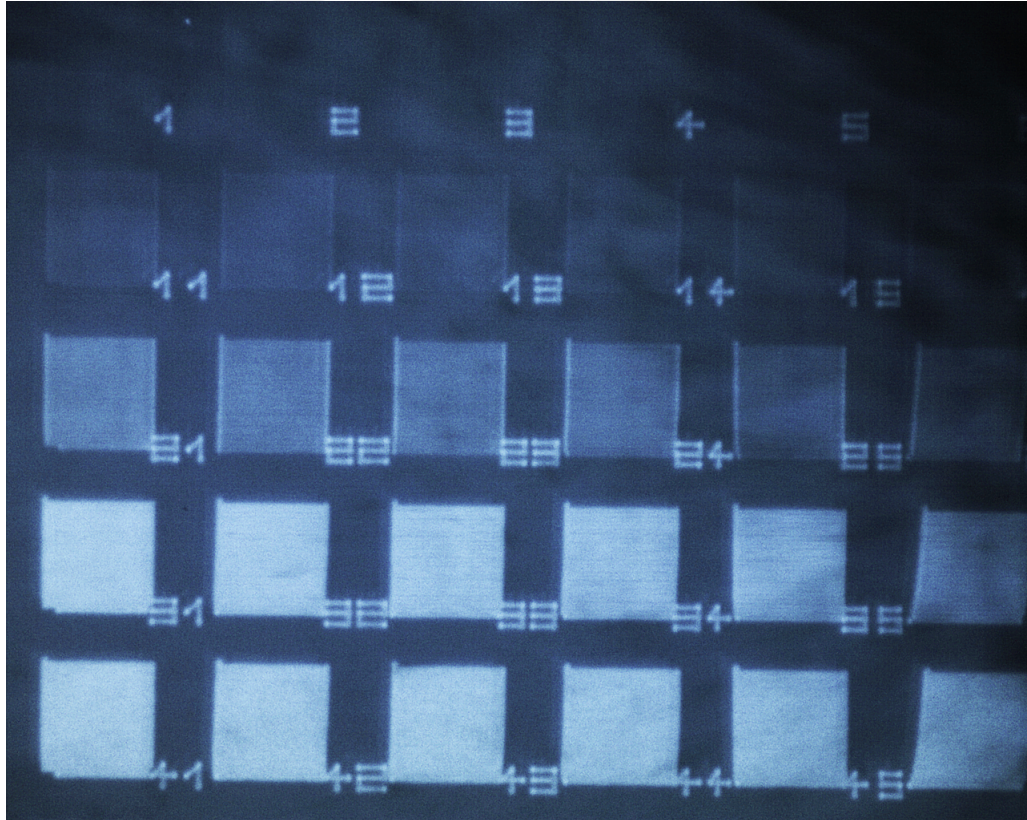


Figure 3.10: A region of a grid of experiments performed to explore the phase space of the NLL structures. The scan speed is increased towards the right while power is increased going down.

Each square in figure 3.10 is a separate experiment and corresponds to a point in the phase space. This procedure allows us to read off the boundaries of the NLL processes in the phase space directly from the experimental figures. The above figure shows the grid scan performed to map the boundaries of Oxidation NLL at a laser repetition rate of 1MHz. A similar grid scan was performed to mark the boundaries of Ablation NLL as well at a pulse repetition rate of 1KHz.

In the above scans, we are varying the laser scan speed and the average laser power, but we want to generate a phase space with the parameters, pulse fluence, and the number of pulses per spot. This translation from the experimental parameters to the desired phase space parameters is carried out as follows.

$$N = \frac{f_R w}{v},$$

and

$$F = \frac{P_{avg}}{A f_R},$$

where $A = \frac{1}{2}\pi(\frac{w}{2})^2$ is the area of beam spot at the focus, w is the beam diameter at the focus, f_R is the repetition rate, v is the scan speed, and P_{avg} is the average laser power incident on the sample. The factor of $\frac{1}{2}$ in the expression for A is due to the beam profile being Gaussian. Thus knowing the repetition rate, beam diameter ($6\mu\text{m}$ in our case), and the scan speed, we can translate our grid experiments to a phase space using the above equations.

The phase space thus generated is shown below. This phase space is for NLL on Cobalt and might be different for different metals.

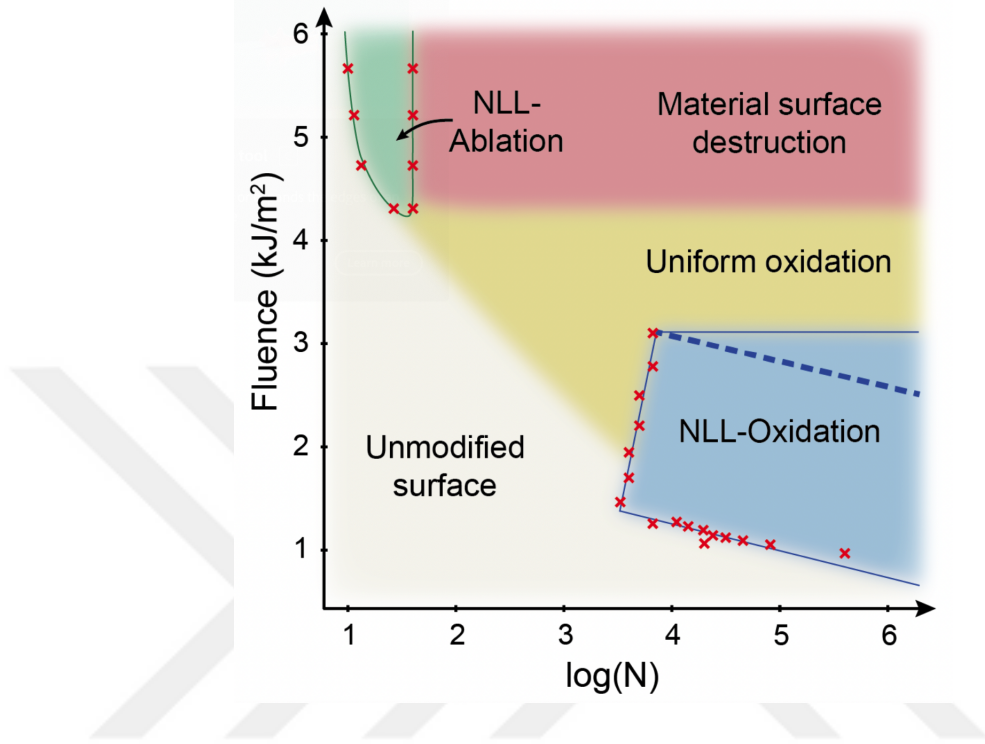


Figure 3.11: Phase space of NLL structures based on pulse fluence and the number of pulses per spot. Ablation NLL structures occupy the top left region of the phase space while Oxidation NLL structures occupy the lower right region. The red crosses represent experiments that mark the boundaries of the NLL regions, the rest of the boundaries are our best guesses for where they should reside and how they might look like.

Where only the experiments marking the boundaries of Oxidation NLL and Ablation NLL have been shown via the red crosses. The positions of boundaries between regions of uniform oxidation, surface destruction, and unmodified surface shown in the figure are our best guesses of where they might reside, but our main purpose was to find the boundaries of the NLL processes in the phase space which the above-mentioned experiments nicely allowed us to do. As expected, we see from the figure that the Oxidation NLL structures are formed at regions of low pulse fluence and high number of pulses per spot while Ablation NLL structures are formed at regions of high pulse fluence and low number of pulses per spot. The scale for N is logarithmic so we can see that the two NLL regions are well separated in terms of the required number of pulses per spot while their separation

in the required pulse fluence is not too broad.

Note that the regions of Oxidation and Ablation NLL are both unbounded from one side in the above figure. In the case of Oxidation NLL, as far as our experiments show, the structures keep forming at higher and higher numbers of pulses as long as a minimum threshold fluence is provided. A bound towards the right might exist and can be checked with lasers having repetition rates high enough to explore that regime. In the case of Ablation NLL, the thickness of our sample restricts further investigation of as to what happens at higher and higher fluence. At a low thickness, pulses having high enough fluence can ablate the metal as a whole but that might not happen with thicker samples. Even if a good chunk of the sample is ablated, the remaining metal might still be modulated with Ablation NLL structures. An investigation at higher thicknesses might be able to provide an upper bound to the Ablation NLL patch of the phase space. Thus due to the limitations of our experimental setup, our results are inconclusive for the regions beyond the patch of the phase space shown in the above figure and further investigations can be made to explore it further. Nevertheless, this phase space provides a deeper understanding of the formation environments of the two NLL processes and might serve as a guide for further NLL investigations.

3.3.5 Tiling the plane

To demonstrate control over the two NLL processes even further, we wanted to generate tiles using both Oxidation and Ablation NLL processes such that they can cover a wider area. Demonstrating such a pattern would help highlight the possibility of using NLL in practical applications. From the experience of generating squares mentioned in section 3.3.3, it seemed reasonable to extrapolate that result in a creative way to generate more intricate patterns. Different orientations of the NLL patterns would provide us with different colors as shown in section 3.3.3. Thus by orienting the NLL structures in different directions with respect to each other, a whole palette of colors could be generated. But in the case of the above-mentioned figure, the Oxidation and Ablation NLL structures

were perpendicular to each other. Will having the same orientation for Oxidation and Ablation NLL structures limit our color palette? To answer that question we formed $300\mu\text{m} \times 300\mu\text{m}$ squares of Oxidation and Ablation NLL structures side by side having parallel orientation and observed them under a stereo microscope. The resulting colors thus observed are shown below.

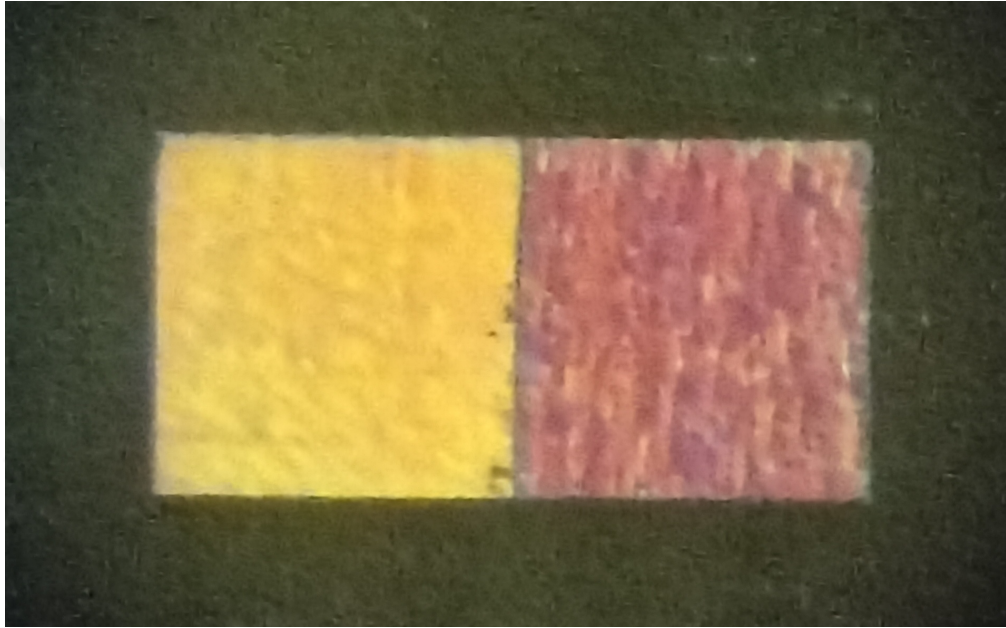


Figure 3.12: Oxidation NLL (red) and Ablation NLL (yellow) structures side by side, having the same orientation. The structures are observed using a Stereo microscope with circular illumination and imaged using a DSLR camera.

As clear from Fig. 3.12, having the same orientation for Oxidation and Ablation NLL structures does not yield the same colors and does not limit our color palette. Armed with this knowledge, and after going over several design ideas, we decided to create a Jigsaw Puzzle shaped design using Oxidation and Ablation NLL structures to demonstrate the tiling capability of NLL. A grey-scale image of the pattern was created and the microscope stage was programmed to create the desired pattern. The resulting pattern as viewed under the Stereo microscope is shown below.

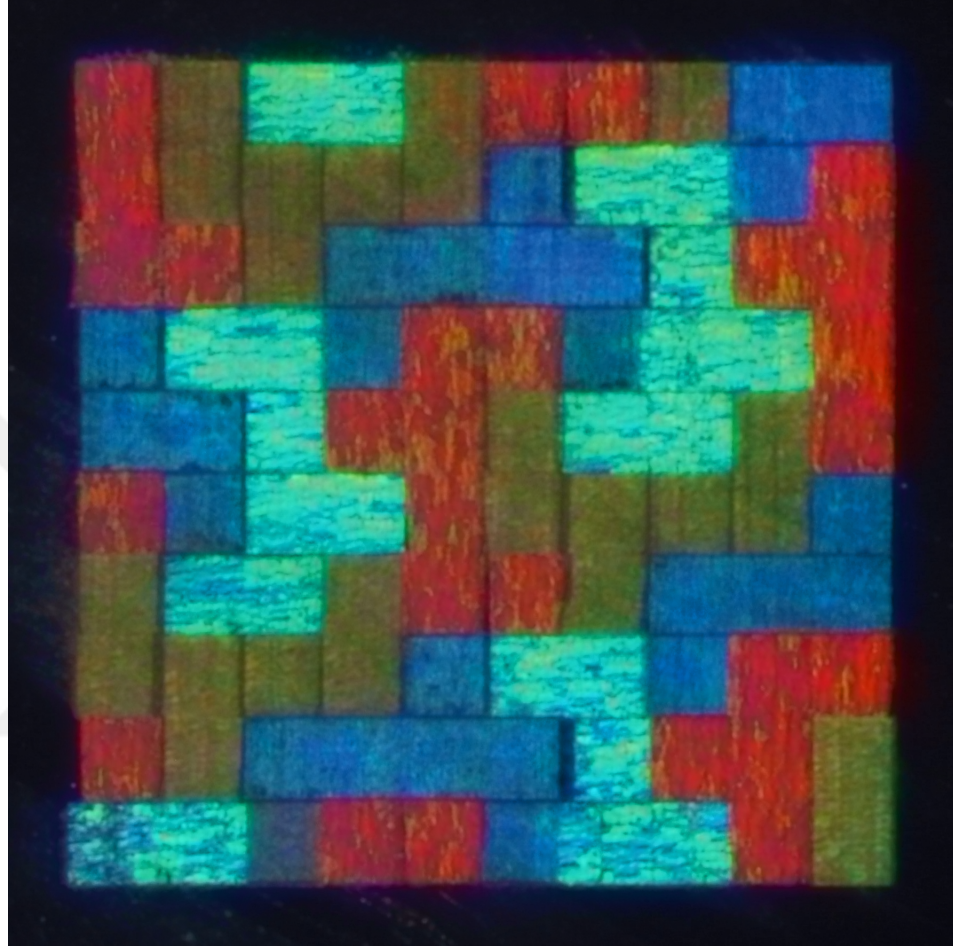


Figure 3.13: A Jigsaw puzzle type pattern created using Oxidation and Ablation NLL structures. The scanning stage is programmed to raster scan the desired pattern. Each square is $100\mu\text{m} \times 100\mu\text{m}$ in size, and created using the parameters described in Fig. 3.6. Oxidation NLL structures formed using vertical polarization are red in color while those formed using horizontal polarization are green. Ablation NLL structures formed using vertical polarization are brown in color while those formed using horizontal polarization are blue.

Figure 3.14, below, shows transitions between different orientations of the NLL structures for both Oxidation and Ablation NLL. In total there are 12 such possible transitions including the transition from parallel structures of one type to parallel structures of the other type, and from horizontal or vertical orientation of one type of structures to the perpendicular orientation of the same or other type. To explore these transitions in more detail, we analyzed them under SEM. The resulting transitions as seen under the SEM are shown below.



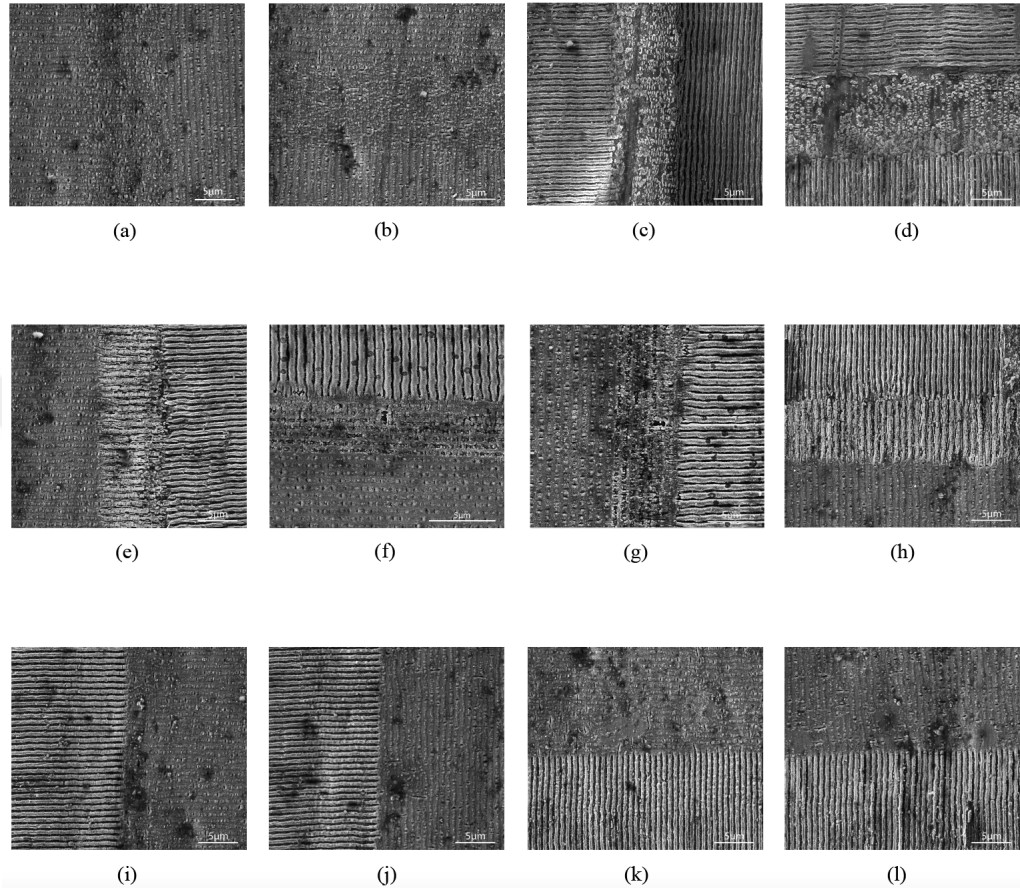


Figure 3.14: Transitions between Oxidation and Ablation NLL on Cobalt for horizontal and vertical polarization of the laser beam. a. Oxidation horizontal polarization to vertical polarization. b. Oxidation vertical polarization to horizontal polarization. c. Ablation vertical polarization to horizontal polarization. d. Ablation horizontal polarization to vertical polarization. e. Oxidation horizontal polarization to Ablation vertical polarization. f. Oxidation horizontal polarization to Ablation horizontal polarization. g. Oxidation vertical polarization to Ablation vertical polarization. h. Oxidation vertical polarization to Ablation horizontal polarization. i. Ablation vertical polarization to Oxidation horizontal polarization. j. Ablation vertical polarization to Oxidation vertical polarization. k. Ablation horizontal polarization to Oxidation horizontal polarization. l. Ablation horizontal polarization to Oxidation vertical polarization. Note: The experiments contain a 8μm-12μm overlap region while going from one process to the other.

3.3.6 Versatility

The above-mentioned experiments are all conducted using Cobalt metal coated on a glass slide. Naturally, the question arises as to whether NLL is a versatile phenomenon, i.e., whether it works on other metals or even non-metals. From the literature, it is clear that both oxidation and Ablation NLL are indeed quite universal. Both processes have been demonstrated on several metals and even a few non-metals such as quartz. But is it possible to obtain them universally 'on the same surface' for all such materials? To answer this question we performed similar analyses as we did for Cobalt for six other materials, including five metals, and Silicon. The materials were coated on glass slides to a similar thickness to that of Cobalt (110nm). They were then processed with the laser to create Oxidation and Ablation NLL structures. The results are shown below.

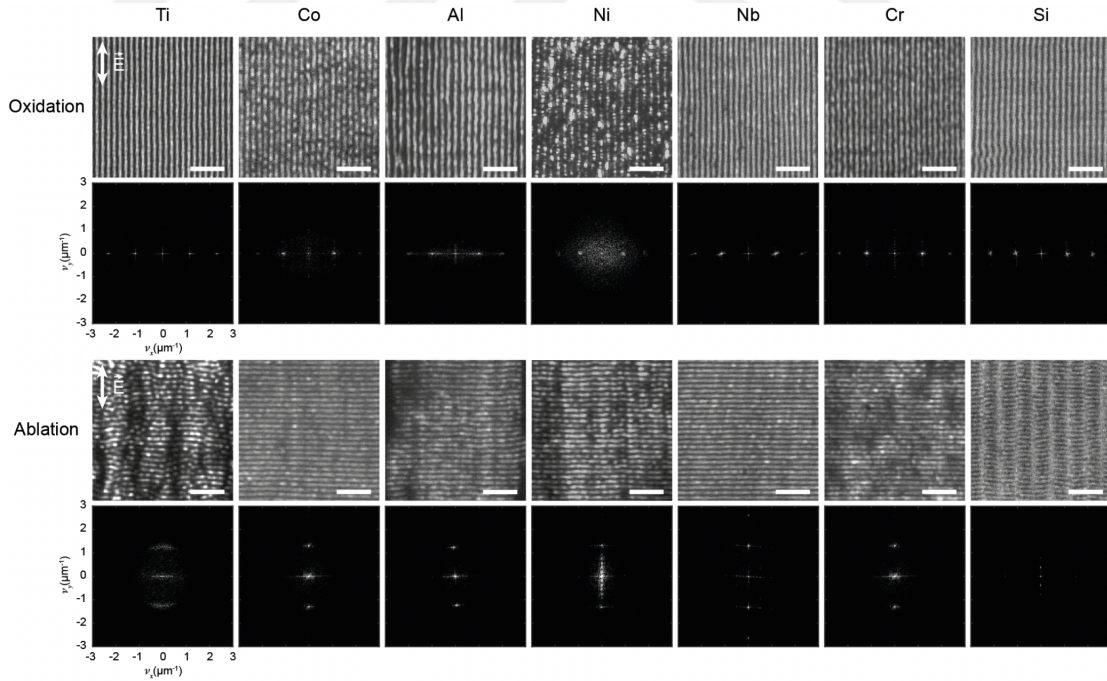


Figure 3.15: Microscope images and their Fourier transforms of Oxidation and Ablation NLL structures formed using the parameters given in table 3.1. The images are taken using a 60x objective.

Figure 3.15, above, shows microscope images of Oxidation and Ablation NLL

on various metals and Silicon, imaged using a 60x magnification objective. The Fourier transforms of the figures were also calculated to get an idea of the structure periods. The periods for Oxidation NLL range from 836nm to 1056nm while that for Ablation NLL range from 686nm to 798nm. The parameters for obtaining the structures shown in figure 3.12 are given in the following table.

Sample Material	Oxidation			Ablation			Thickness (nm)
	Scanning Speed ($\mu\text{m/s}$)	Number of pulses per spot	Pulse Fluence (KJ/m^2)	Scanning Speed ($\mu\text{m/s}$)	Number of pulses per spot	Pulse Fluence (KJ/m^2)	
Cobalt	30	200,000	0.424	200	60	2.12	110
Niobium	20	300,000	0.424	200	60	2.12	120
Nickel	10	600,000	0.353	250	48	2.83	230
Chromium	30	200,000	0.424	200	60	2.12	177
Aluminum	10	600,000	0.424	200	60	2.48	200
Titanium	20	300,000	0.396	250	12	3.40	135
Silicon	10	300	7.074	250	12	7.07	200

Table 3.1: Parameters for obtaining Oxidation and Ablation NLL for various materials.

As evident from table 3.1, we see that not only the process of NLL is universal but the conditions in which it manifests itself are also quite universal, at least in terms of laser parameters. For metals to form Oxidation NLL, they seem to all require hundreds of thousands of pulses incident per spot while tens of pulses per spot are required for Ablation NLL. The required pulse fluence is around 0.4kJ/m^2 for Oxidation NLL and around 2.5kJ/m^2 for Ablation NLL. This can lead one to speculate that the phase space might be similar for all metals but that need not be the case since the above-mentioned parameters correspond to experiments that are a single point in their respective phase spaces and the entire phase space might turn out to be quite different for each metal. The different thicknesses required for different metals are also expected due to the fact that the skin depth for the laser wavelength varies for each metal and affects the formation of both Oxidation and Ablation NLL. Silicon is a noticeable exception here, the parameters for Silicon are quite different compared to the metals, but that is expected since it is a semiconductor. The mere fact that both types of NLL can be obtained in Silicon is fascinating since most of the work on NLL has focused on patterning the surface of metals. Silicon turned out to be even more interesting than metals in our investigations due to the presence of a third type of NLL,

which we will discuss more in Chapter 5.

The figure below shows the SEM images for both Oxidation and Ablation NLL obtained using the parameters mentioned in Table 3.1.

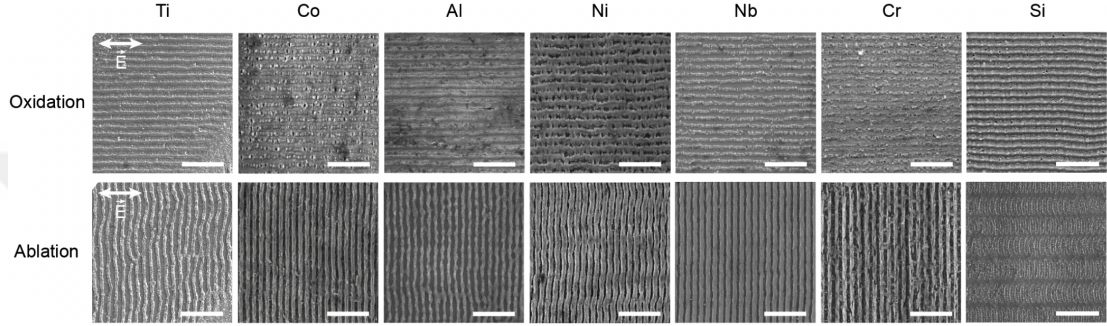


Figure 3.16: SEM images of Oxidation and Ablation NLL structures formed using the parameters given in table 3.1. The scale bar is $5\mu\text{m}$.

To study the effect of thickness in a bit more detail, we experimented with various thicknesses for the different elements. It was observed that thickness plays quite a significant role in the regularity of the structures. Even though both Oxidation and Ablation NLL can be obtained simultaneously on the same thickness for a thick enough sample, it might not be the optimal thickness for either of them. Optimal here refers to the regularity of the structures. The effect of thickness is more pronounced for Oxidation NLL. The regularity has an inverse relationship with the thickness. As the thickness increases, the Oxidation NLL structures tend to get wavy, bifurcations occur with a higher probability, and the structures might occasionally experience discontinuities. This might be caused due to a change in the feedback profile from the existing structures induced by the change in the effective refractive index. For samples thinner than the laser wavelength, the laser beam experiences an effective refractive index due to interaction with the metal and glass simultaneously. As the thickness increases, it will cause this effective refractive index to change which might be the cause of the waviness of the structures. However, more investigations need to be carried out to get a definitive answer.

The figure below shows microscope images, taken using a 100x objective, of the Oxidation and Ablation NLL structures formed at optimal thicknesses.

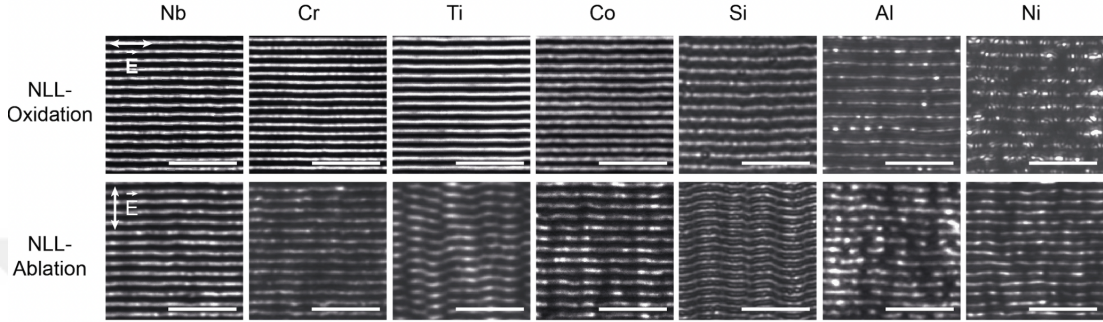


Figure 3.17: Oxidation and Ablation NLL structures at optimal thicknesses as shown under a 100x microscope objective. Nb, Cr, Ti and Co, have film thickness of 60nm while that for Si, Al, and Ni are the same that the ones given in Table 3.1.

Here, the thicknesses for the two NLL are no longer the same for most elements but are optimized for each type of NLL. We can clearly see that the Oxidation NLL structures for most elements become more regular at lower thicknesses. However, for some elements, a lower thickness can have an adverse effect. For instance, in the case of Aluminum and Nickel, Oxidation NLL structures could only be obtained in thicker samples.

The above discussion is by no means an exhaustive account of the complete versatility of the NLL processes. We only used elements available to us for coating on a glass slide and more elements can be added to the list in further investigations. However, our investigation does bring to light the ubiquitousness of the NLL processes and how different NLL processes can coexist on different surfaces. This discussion can thus act as a guide for possible future investigations on the universality of the NLL processes.

3.3.7 Applications

Numerous applications of the NLL processes have been talked about in the literature. The applications exploit the possibility of large-scale surface patterning using NLL structures. They are used to make gratings, pattern dental equipment, improve the efficiency of solar cells, etc. Here we demonstrate a few applications that have not been mentioned in the literature to the best of our knowledge.

We developed a temperature sensor using Oxidation NLL structures patterning a metal surface coated on a Polymer. The polymer used was a heat-resistant Kapton tape. The tape was first attached to a glass slide and was then coated over by a 200nm thick layer of Titanium metal. The sample was then patterned with Oxidation NLL structures using the same parameters as mentioned in Table 3.1. The structures on the metal-coated polymer are similar to those obtained with the metal-coated glass slide. However, due to the differing coefficients of thermal expansion between the polymer (20×10^{-6}) and the metal (8.5×10^{-6}), the polymer expands more than the metal causing the metal surface to crack along with being oxidized. The resulting structures look as follows:

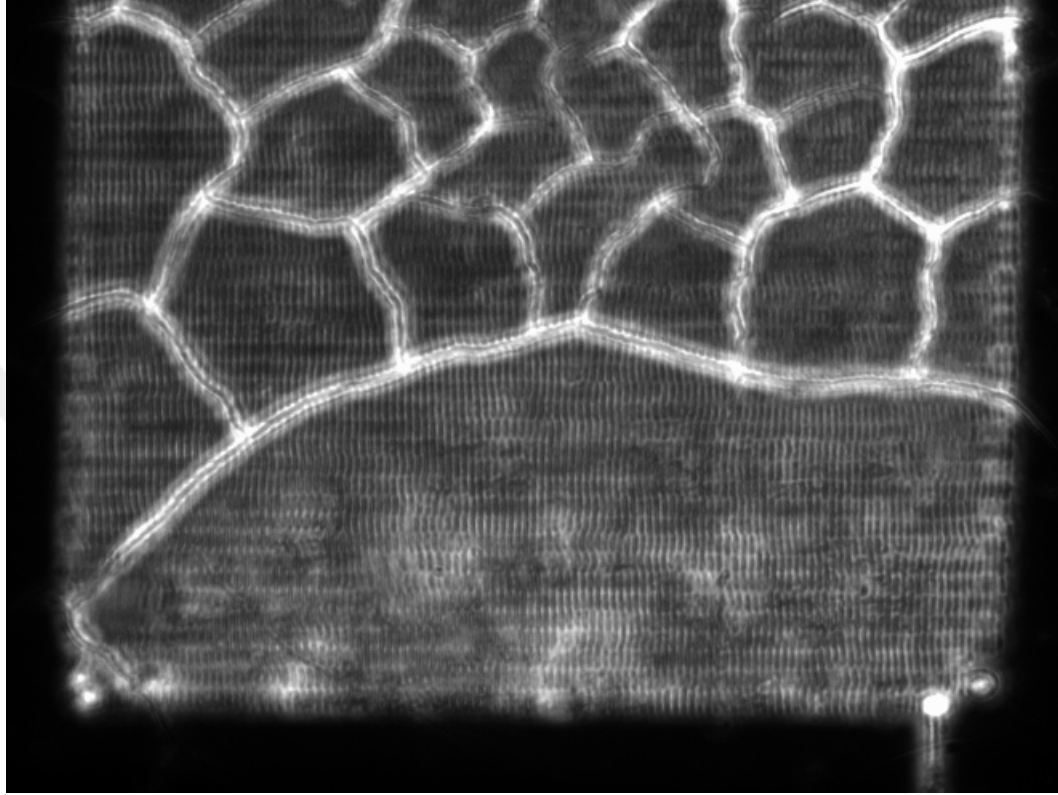


Figure 3.18: Oxidation NLL structures formed on Kopton tape, a heat resistant polymer. The structures are formed using the parameters mentioned in table 3.1.

We then coated 110nm Cobalt on Kapton tape in a similar fashion as shown above. We patterned a 2mm x 2mm square of Cobalt Oxide structures on the metal surface. We then placed it on top of a Peltier Cell, which changes temperature depending on the change in applied voltage. The whole setup was then placed under a Stereo microscope. The sample was heated up to a temperature of 100°C and then subsequently cooled and any changes to the sample were observed via the microscope. The effect of temperature on the light reflected from the structures is shown in the following figure.

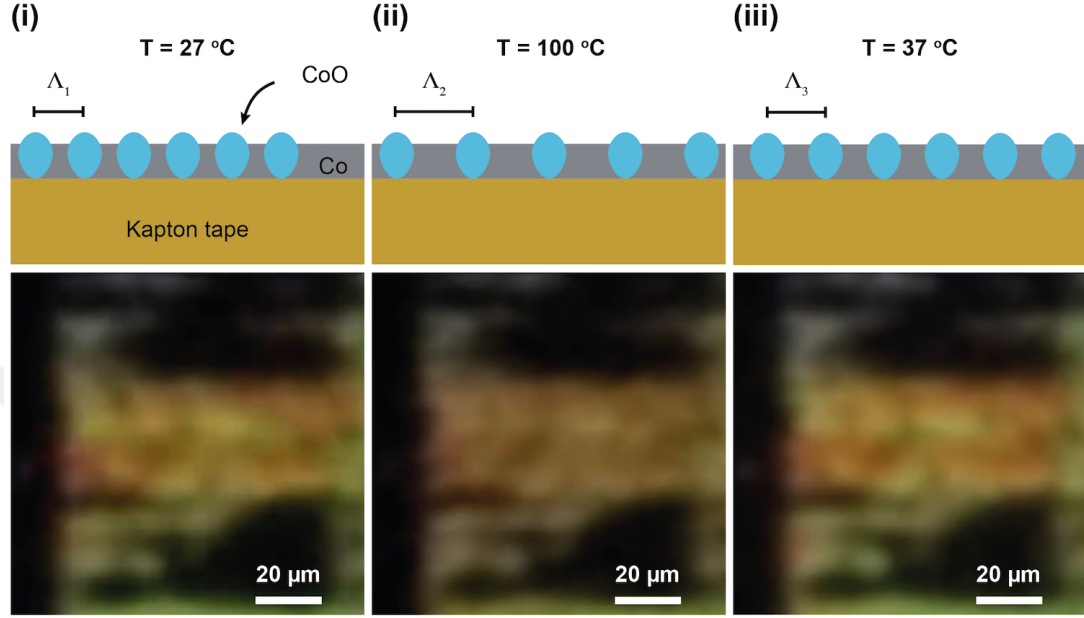


Figure 3.19: Temperature sensor composed of Oxidation NLL structures on 110 thick Cobalt coated on Kapton tape. As the temperature changes, it causes the period of the structures to change which in turn changes the diffraction pattern and hence the color of the structures. This process can be used to measure temperature.

A significant color change can be observed with a change in temperature. To quantify the change in color, we observe how the amount of red in the images changes as the temperature varies. Plotting the average amount of red in the pixels of the images taken from the microscope, we can make the following graph.

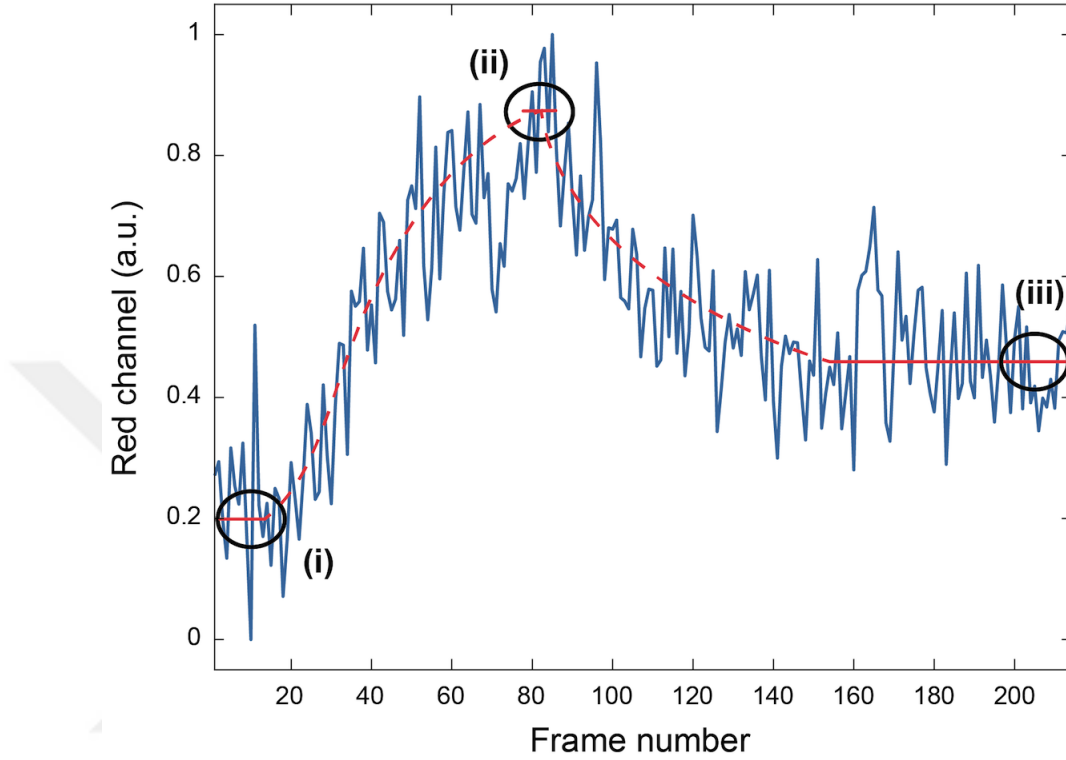


Figure 3.20: Red channel in each frame. We can see that the sample became redder when heated.

The graph shown in Fig. 3.20, was formed by analyzing the red values in each frame of a video showing the heating and cooling of the sample using the Peltier Cell. From the above graph, it is clear that as the temperature increases, the NLL structures undergo an expansion that changes the color of the reflected light, and as the temperature is decreased, the structures regain their initial shape causing the initial colors to return. Associating the color with the temperature can allow us to use this setup as a temperature sensor. Note that this is just a proof-of-concept device and can be improved significantly for use in commercial applications.

The above experiment shows the possibility of creating NLL structures on a polymer, which is technologically important in itself. This can pave the way for bendable temperature sensors and wearable electronics among other applications.

Another application involving the modification of surfaces using NLL structures for useful purposes is Wettability. The NLL structures are formed by modification of the material surface. These modifications are not only chemical but also change the physical properties of the surface, some examples of which we have seen above. One of the physical properties of the surface that can change due to NLL is the ability of water to spread over the material surface, known as Wettability. In our investigations, we have observed that Oxidation NLL has a significant effect on the wettability properties of the material. The Wettability experiments were performed using Silicon as the sample material. Water droplets dropped on untreated Silicon form a contact angle of 70° with the Silicon surface. Once treated with Oxidation NLL, the contact angle decreases significantly to 10° showing that treatment with NLL causes the Silicon surface to become hydrophilic. To make the surface hydrophobic, the NLL-processed sample is coated with Octafluorocyclobutane, a polymer known for its hydrophobic properties. Upon treatment with C_4F_8 the contact angle increases significantly to 180° , showing that the sample has become significantly hydrophobic. The figure below shows the hydrophilicity and the hydrophobicity of the Silicon sample in action.

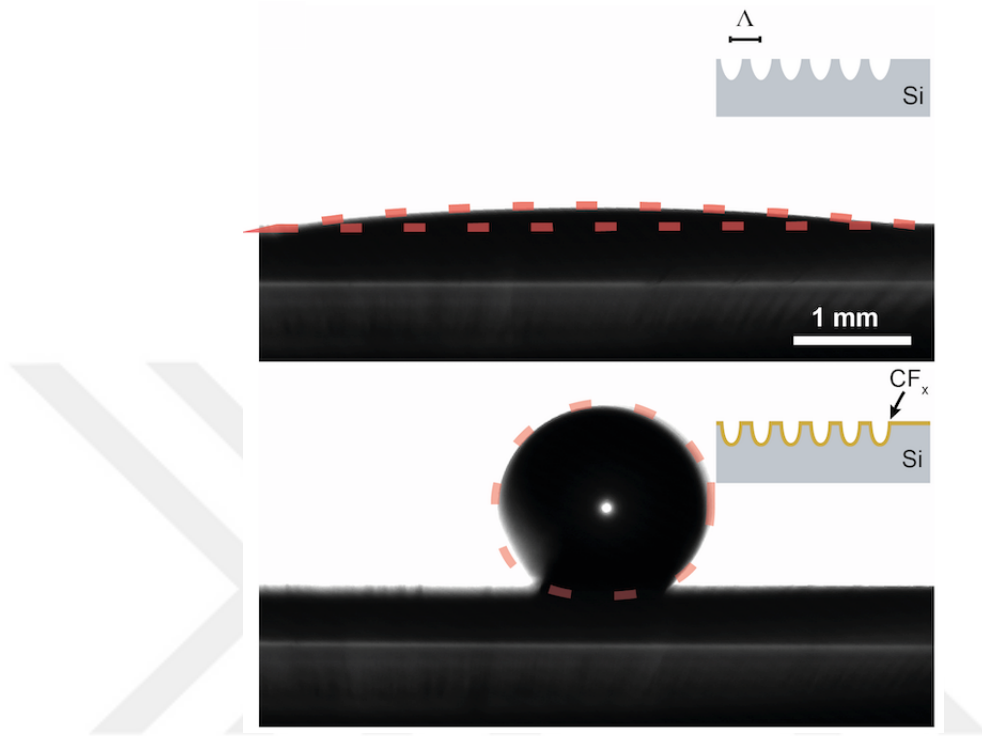


Figure 3.21: (Top) The hydrophilic Oxidation NLL structures formed on Si surface. (Bottom) The structures are then coated with 8 nm of C_4F_8 , this makes the structures super hydrophobic.

An investigation was also carried out as to how the thickness of the polymer layer influences the hydrophobicity of the sample. The following graph shows the results of that analysis.

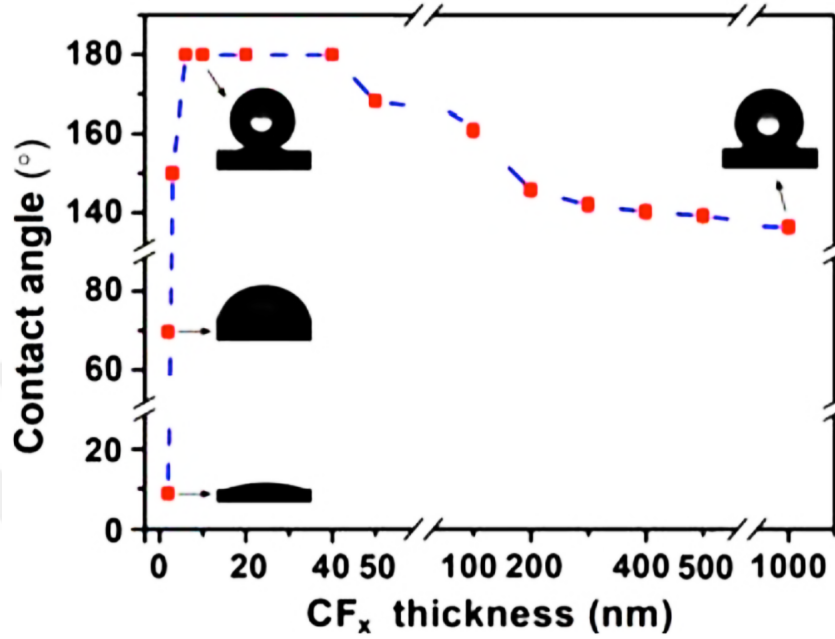


Figure 3.22: The hydrophobicity of Oxidation NLL structures vs the thickness of the C_4F_8 coating.

As evident, the hydrophobicity initially increases significantly with increasing the thickness of the C_4F_8 layer. However, as the polymer thickness is increased beyond 40nm, a drop in the hydrophobicity is observed.

Lastly, it was observed that if this C_4F_8 treated sample was again treated with NLL, it causes the polymer layer to vaporize, exposing the hydrophilic NLL-treated layer. This thus allows hydrophobic and hydrophilic patches to coexist on the material surface. This in turn allows for the possibility of constructing microchannels that can guide water on the material surface along a well-defined path.

As a final application of NLL, we tried to mimic the colors of nature in the lab. The results are shown below.

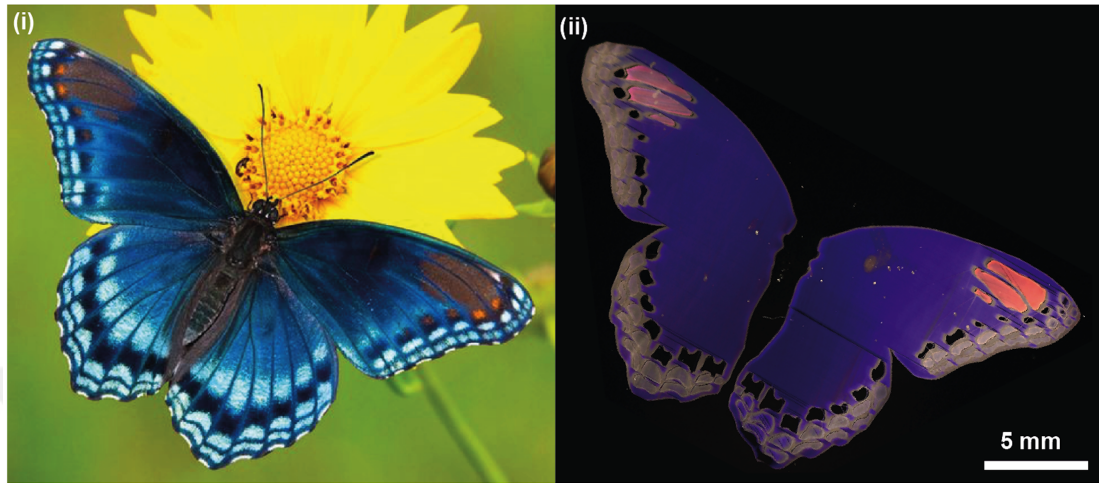


Figure 3.23: (i) A Red-spotted Purple Admiral Butterfly (ii) Our rendition of the Admiral butterfly in the lab, created using Ablation NLL on 110nm Cobalt surface. The different colors are obtained by varying the polarization angle of the laser beam.

The above-mentioned applications are just the tip of the iceberg of the possible applications of NLL. Applications till now have focused on using Oxidation or Ablation NLL separately. Our work thus opens up a new frontier of possible applications in which Oxidation and Ablation NLL can be applied simultaneously to obtain desired material properties.

Chapter 4

The Doppler Effect

4.1 Theory

In the above sections, we have described the process of the formation of NLL structures due to oxidation and ablation of the metal sample caused by the incident laser pulses. In the analysis, we assumed the normal incidence of the laser beam on the metal surface. But what if the laser is not incident normally? We will investigate the answer to this question in the case of oxidation NLL structures in this section. As we shall see, a change in the angle of incidence causes the period of the resulting structures to change. Interestingly, by changing the angle of incidence, we can cause the period of the structures to increase or decrease compared to the case of normal incidence. This is reminiscent of the change in frequency of a wave with the relative motion between emitter and observer, known as the Doppler effect. We will see that the equation for the period of the resulting structures will provide us with a direct analogy with the Doppler effect. The schematic of the Doppler effect in NLL is shown in the figure below [17].

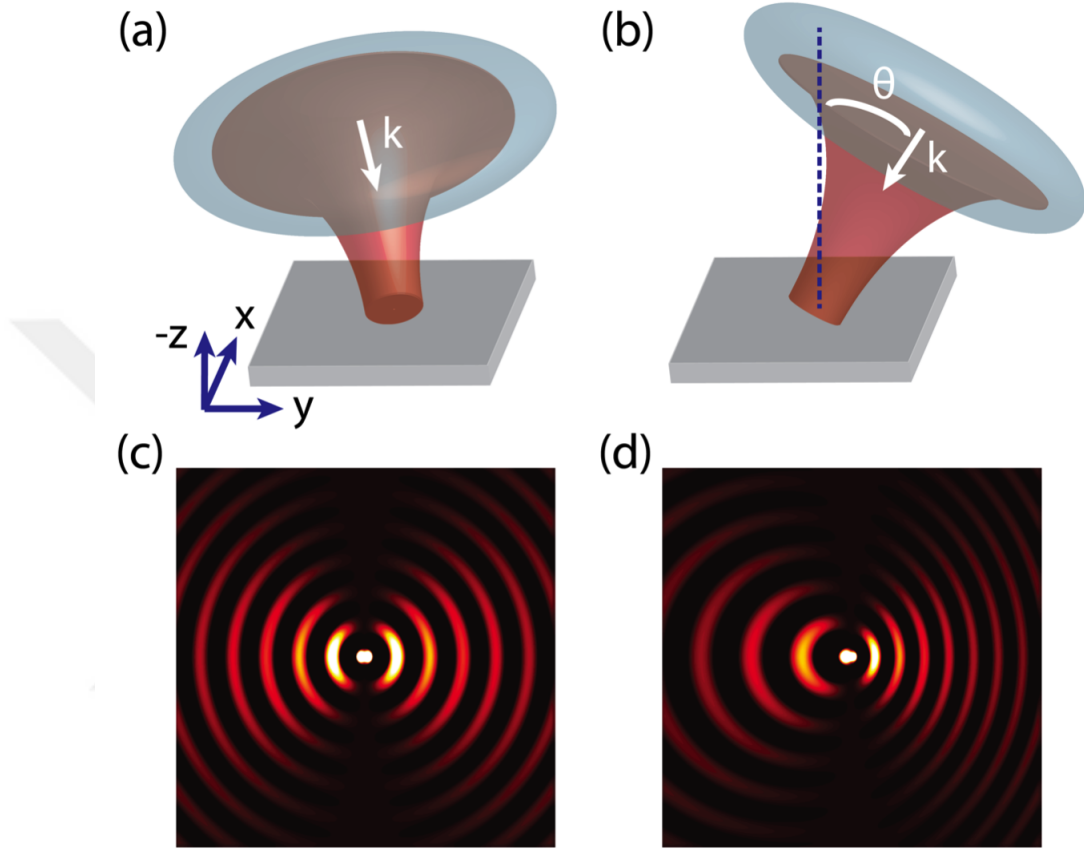


Figure 4.1: (a)Schematic showing the normal incidence of the laser beam on the sample. (b)Schematic showing the non-normal incidence of the laser beam with a tilt angle θ from the $-z$ axis. (c)Surface intensity profile due to normally incident laser beam on a defect at the center. (d)(c)Surface intensity profile due to a tilted laser beam on a defect at the center.

Initially, we consider the laser beam to be normally incident on the x - y plane. Assuming linear polarization, we get the following components for the incident $\vec{E}$ field.

$$E_x = E_0 \cos(\beta), \quad (4.1)$$

$$E_y = E_0 \sin(\beta), \quad (4.2)$$

where β be the polarization angle defined w.r.t x-axis.

To incorporate the effect of tilt we see that, depending on the polarization of the incident light, the k-vector contribution on the x-y plane will vary because of the introduction of the z-component caused by the tilt. Thus, if the beam is tilted towards the x-axis we get the magnitudes of the $\vec{E}$ field components as follows.

$$E_x = E_0 \cos(\beta) \cos(\Phi_x), \quad (4.3)$$

$$E_y = E_0 \sin(\beta), \quad (4.4)$$

where Φ_x is the angle by which the beam is tilted away from the z-axis and towards the x-axis. Similarly, if the beam is tilted in the y-direction, we get:

$$E_x = E_0 \cos(\beta), \quad (4.5)$$

$$E_y = E_0 \sin(\beta) \cos(\Phi_y), \quad (4.6)$$

where Φ_y is the angle by which the beam is tilted away from the z-axis and towards the y-axis.

In the general case of an arbitrary tilt angle, magnitudes of both E_x and E_y will change as follows.

$$E_x = E_0 \cos(\beta) \cos(\Phi_x), \quad (4.7)$$

$$E_y = E_0 \sin(\beta) \cos(\Phi_y), \quad (4.8)$$

we will use this general case in our upcoming analysis to get a relation between the structure period and an arbitrary tilt angle.

Now we will calculate the scattered field in the far field, also component-wise, using equations (2.15) and (2.16).

$$\begin{aligned}
E_{scat_x} &= \iint \xi h(x', y') \frac{e^{-ikr}}{r} [E_x \cos^2(\theta) - E_y \sin(\theta) \cos(\theta)] dx' dy' \\
&= \iint E_0 e^{\frac{-|r-r'|^2}{2w^2}} e^{-ik(\sin(\Phi_x)x' + \sin(\Phi_y)y')} h(x', y') \frac{e^{-ikr}}{r} \\
&\quad [\cos(\beta) \cos(\Phi_x) \cos^2(\theta) - \sin(\beta) \cos(\Phi_y) \sin(\theta) \cos(\theta)] dx' dy',
\end{aligned} \tag{4.9}$$

where θ is the polar angle defined as $\theta = \tan^{-1}(\frac{x-x'}{y-y'})$, $r = \sqrt{(x-x')^2 + (y-y')^2}$, and in the second line we have absorbed all constants into E_0 . Due to Rayleigh scattering from the defects caused by the k_x and k_y components of the wave vector, we will get a phase term in the scattering integral which depends on the tilt angle as shown above.

For simplicity, we only focus on scattering due to a single defect at the origin, thus we can take the height function as a delta function at the origin:

$$h(x', y') = \delta(x', y'). \tag{4.10}$$

This gives:

$$E_{scat_x} = E_0 e^{\frac{-r^2}{2w^2}} \frac{e^{-ikr}}{r} \cos(\theta) [\cos(\beta) \cos(\Phi_x) \cos(\theta) - \sin(\beta) \cos(\Phi_y) \sin(\theta)]. \tag{4.11}$$

Let

$$[\cos(\beta) \cos(\Phi_x) \cos(\theta) - \sin(\beta) \cos(\Phi_y) \sin(\theta)] = B(\beta, \theta, \Phi_x, \Phi_y) = B. \tag{4.12}$$

The x-component of the scattered field is thus given by:

$$E_{scat_x} = E_0 e^{\frac{-r^2}{2w^2}} \frac{e^{-ikr}}{r} \cos(\theta) B. \tag{4.13}$$

Similarly, for the scattered field in the y-direction, E_{scat_y} , we obtain:

$$E_{scat_y} = E_0 e^{\frac{-r^2}{2w^2}} \frac{e^{-ikr}}{r} (-\sin(\theta)) B. \quad (4.14)$$

For the incident field, the tilt will not only change the magnitude of the $\vec{E}$ field components but will also give it a phase factor due to the x-y components of the wave vector as shown below.

$$E_{inc_x} = E_0 e^{\frac{-r^2}{2w^2}} e^{-ik(\sin(\Phi_x)x + \sin(\Phi_y)y)} \cos(\beta) \cos(\Phi_x), \quad (4.15)$$

and

$$E_{inc_y} = E_0 e^{\frac{-r^2}{2w^2}} e^{-ik(\sin(\Phi_x)x + \sin(\Phi_y)y)} \sin(\beta) \cos(\Phi_y). \quad (4.16)$$

The total surface electric field is thus given by:

$$\begin{aligned} E_{tot_x} &= E_{inc_x} + E_{scat_x} \\ &= E_0 e^{\frac{-r^2}{2w^2}} \left[e^{-ik(\sin(\Phi_x)x + \sin(\Phi_y)y)} \cos(\beta) \cos(\Phi_x) + \frac{e^{-ikr}}{r} \cos(\theta) B \right], \end{aligned} \quad (4.17)$$

and

$$\begin{aligned} E_{tot_y} &= E_{inc_y} + E_{scat_y} \\ &= E_0 e^{\frac{-r^2}{2w^2}} \left[e^{-ik(\sin(\Phi_x)x + \sin(\Phi_y)y)} \sin(\beta) \cos(\Phi_y) - \frac{e^{-ikr}}{r} \sin(\theta) B \right]. \end{aligned} \quad (4.18)$$

The expression for the total Intensity then becomes:

$$I_{tot} = |E_{tot_x}|^2 + |E_{tot_y}|^2, \quad (4.19)$$

where

$$\begin{aligned} |E_{tot_x}|^2 &= E_0^2 e^{\frac{-r^2}{w^2}} \left[\cos^2(\beta) \cos^2(\Phi_x) + \cos^2(\theta) \frac{B^2}{r^2} + \frac{e^{ik(\sin(\Phi_x)x + \sin(\Phi_y)y - r)}}{r} \right. \\ &\quad \left. \cos(\theta) \cos(\beta) \cos(\Phi_x) B + \frac{e^{-ik(\sin(\Phi_x)x + \sin(\Phi_y)y - r)}}{r} \cos(\theta) \cos(\beta) \cos(\Phi_x) B \right]. \end{aligned} \quad (4.20)$$

To simplify the above expression, we ignore the $1/r^2$ term and turn the sum of exponentials into cosines:

$$|E_{tot_x}|^2 = E_0^2 e^{\frac{-r^2}{w^2}} [\cos^2(\beta) \cos^2(\Phi_x) + 2 \cos(\theta) \cos(\beta) \cos(\Phi_x) \frac{B}{r} \cos[k(\sin(\Phi_x)x + \sin(\Phi_y)y - r)]], \quad (4.21)$$

similarly,

$$|E_{tot_y}|^2 = E_0^2 e^{\frac{-r^2}{w^2}} [\sin^2(\beta) \cos^2(\Phi_y) - 2 \sin(\theta) \sin(\beta) \cos(\Phi_y) \frac{B}{r} \cos[k(\sin(\Phi_x)x + \sin(\Phi_y)y - r)]]. \quad (4.22)$$

Thus,

$$\begin{aligned} I_{tot} &= |E_{tot_x}|^2 + |E_{tot_y}|^2 \\ &= E_0^2 e^{\frac{-r^2}{w^2}} [\cos^2(\beta) \cos^2(\Phi_x) + 2 \cos(\theta) \cos(\beta) \cos(\Phi_x) \frac{B}{r} \cos[k(\sin(\Phi_x)x + \sin(\Phi_y)y - r)]] \\ &\quad + E_0^2 e^{\frac{-r^2}{w^2}} [\sin^2(\beta) \cos^2(\Phi_y) - 2 \sin(\theta) \sin(\beta) \cos(\Phi_y) \frac{B}{r} \cos[k(\sin(\Phi_x)x + \sin(\Phi_y)y - r)]] \quad (4.23) \\ &= E_0^2 e^{\frac{-r^2}{w^2}} [\cos^2(\beta) \cos^2(\Phi_x) + \sin^2(\beta) \cos^2(\Phi_y) + \\ &\quad 2 \frac{B}{r} \cos[k(\sin(\Phi_x)x + \sin(\Phi_y)y - r)] (\cos(\theta) \cos(\beta) \cos(\Phi_x) \\ &\quad - \sin(\theta) \sin(\beta) \cos(\Phi_y))]. \end{aligned}$$

Making the following substitution,

$$[\cos(\beta) \cos(\Phi_x) \cos(\theta) - \sin(\beta) \cos(\Phi_y) \sin(\theta)] = B,$$

gives,

$$I_{tot} = E_0^2 e^{\frac{-r^2}{w^2}} [\cos^2(\beta) \cos^2(\Phi_x) + \sin^2(\beta) \cos^2(\Phi_y)] + 2 \frac{B^2}{r} \cos[k(\sin(\Phi_x)x + \sin(\Phi_y)y - r)]. \quad (4.24)$$

Using polar coordinates we can replace $x = r \cos(\theta)$ and $y = r \sin(\theta)$. Also, cosine is an even function, so we can write the above expression as follows:

$$I_{tot} = E_0^2 e^{\frac{-r^2}{w^2}} [\cos^2(\beta) \cos^2(\Phi_x) + \sin^2(\beta) \cos^2(\Phi_y)] + 2 \frac{B^2}{r} \cos[kr(1 - \cos(\theta) \sin(\Phi_x) - \sin(\theta) \sin(\Phi_y))]. \quad (4.25)$$

The regions where the E-field constructively interferes experience the highest intensity and allow for the formation of NLL structures, so we are looking for the maximas of the intensity profile, such that:

$$\frac{dI_{tot}}{dr} = 0, \quad (4.26)$$

this gives:

$$\frac{dI_{tot}}{dr} = E_0^2 e^{\frac{-r^2}{w^2}} \left(\frac{-2r}{w^2} \right) [\cos^2(\beta) \cos^2(\Phi_x) + \sin^2(\beta) \cos^2(\Phi_y)] + 2 \frac{B^2}{r} \cos[kr(1 - \cos(\theta) \sin(\Phi_x) - \sin(\theta) \sin(\Phi_y))]. \quad (4.27)$$

After taking the derivative the above expression will include r^{-1} and r^{-2} terms which we will ignore. The expression then becomes:

$$\frac{dI_{tot}}{dr} = E_0^2 e^{\frac{-r^2}{w^2}} \left(\frac{-2}{w^2} \right) [r \cos^2(\beta) \cos^2(\Phi_x) + r \sin^2(\beta) \cos^2(\Phi_y)] + 2B^2 \cos[kr(1 - \cos(\theta) \sin(\Phi_x) - \sin(\theta) \sin(\Phi_y))], \quad (4.28)$$

assuming small r , we get:

$$\frac{dI_{tot}}{dr} = E_0^2 e^{\frac{-r^2}{w^2}} \left(\frac{-4}{w^2} \right) B^2 \cos[kr(1 - \cos(\theta) \sin(\Phi_x) - \sin(\theta) \sin(\Phi_y))] = 0. \quad (4.29)$$

The above expression holds when the argument of the cosine is an odd multiple of $\frac{\pi}{2}$, thus:

$$kr(1 - \cos(\theta) \sin(\Phi_x) - \sin(\theta) \sin(\Phi_y)) = (2n + 1) \frac{\pi}{2}, \quad (4.30)$$

where n is a non-negative integer. The above expression gives the extreme points w.r.t r for the intensity profile, for the maxima points, we take two alternating points as follows:

$$kr(1 - \cos(\theta) \sin(\Phi_x) - \sin(\theta) \sin(\Phi_y)) = (4n + 1) \frac{\pi}{2}, \quad (4.31)$$

$$r = \frac{(4n + 1) \frac{\pi}{2}}{\frac{2\pi}{\Lambda}(1 - \cos(\theta) \sin(\Phi_x) - \sin(\theta) \sin(\Phi_y))}. \quad (4.32)$$

The period of the structures is thus given as:

$$\Lambda' = r_2 - r_1 \quad (4.33)$$

$$\Lambda' = \frac{\Lambda}{1 - \cos(\theta) \sin(\Phi_x) - \sin(\theta) \sin(\Phi_y)}. \quad (4.34)$$

The wavelength of the E-field incident on the surface is given by Λ while the period of the structures is given by Λ' .

For a unidirectional tilt angle, for instance Φ_x , the analogy with the Doppler Effect is clearer. Taking $\Phi_y = 0$ gives:

$$\Lambda' = \frac{\Lambda}{1 - \sin(\Phi_x) \cos(\theta)}. \quad (4.35)$$

Replacing $\sin(\Phi_x)$ by v/c in the above equation, we obtain the expression for the Doppler effect for the light source and the observer having a relative velocity of ' v ', such that:

$$\Lambda' = \frac{\Lambda}{1 - \frac{v}{c} \cos(\theta)}. \quad (4.36)$$

We see that the Doppler Effect in NLL and that in wave dynamics are analogous to each other if we consider the speed of the waves to be analogous to the sine of the tilt angle. Thus in light of this analogy, we see that having a tilt away from the scan direction corresponds to the source and the observer moving away from each other in the classical Doppler effect while having a tilt toward the scan direction corresponds to the observer and the source moving towards each other.

4.2 Simulations

Eq. 4.25 gives the surface intensity profile in the general case of non-normal incidence of the laser beam on the sample surface. It is a more general version of equation 2.24, which can be obtained from eq. 4.25 by taking the tilt angles to zero. However, it needs to be noted that the analysis leading to eq. 4.25 ignores the effects of the near field, including which, can make a generalized analytical model like the one above, quite complicated. In numerical simulations, however, it is simpler to simulate the general model while including the near field as well. One simply needs to take into account the fact that the magnitudes of the Electric Field components will be modified depending on the tilt angle. The scattered waves will also experience a phase shift which depends on the tilt angle, this will change the interference pattern on the surface and allow for the formation of structures that seem to undergo the Doppler effect.

Using the above-mentioned modifications of the model for NLL discussed in ch. 2, we can simulate the effect of non-normal incidence of the laser beam on the sample surface. As expected from our discussion above, after running some simulations one can observe the dependence of period on the scan direction. If the beam is tilted away from the scan direction, the period of the structures is larger than that obtained with normal incidence while if it is tilted towards the scan direction then the structure period is smaller. The figure below shows simulations demonstrating this effect.

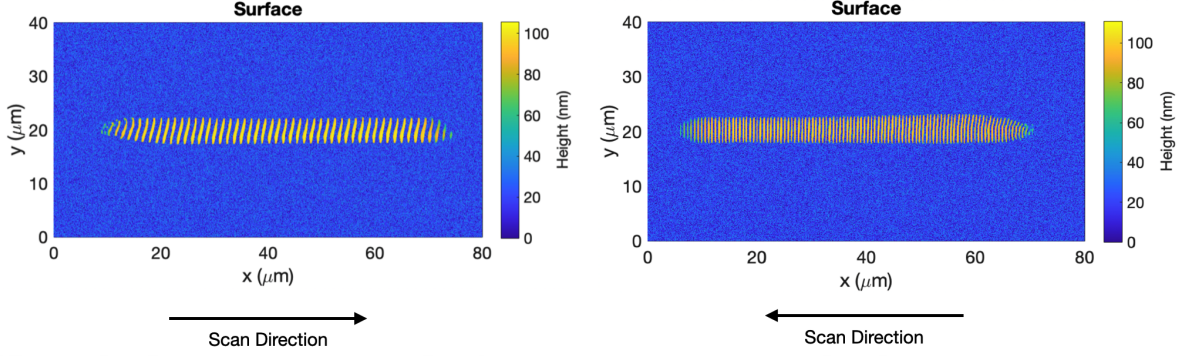


Figure 4.2: Demonstrating Temporal Symmetry Breaking. (Left) The tilt angle is away from the scan direction giving rise to larger periods of the structures. (Right) The structure period is small when the beam is scanned in the direction of the tilt angle.

This is an instance of temporal symmetry breaking. If one were to scan in the $+x$ direction say with a tilt towards the $-x$ direction, the structure period would be larger. But now if the movie is run backward, then the structures obtained should be smaller in period since the scan direction and the tilt direction are both along the $-x$ direction. This dependence on scan direction thus gives rise to temporal symmetry breaking.

Equation 4.34 gives an expression for the new period of the structures once some tilt has been introduced in the beam incidence. The new expression of the period depends on three variables, the x and y components of the tilt, and the polar angle. One can get an insight into the behavior of the structure period with tilt by considering the x and y tilt separately. Taking the tilt in the y -direction to be zero, we get the effect of the x -direction tilt on the period of the structures and vice-versa. Plots of both of these cases are shown below.

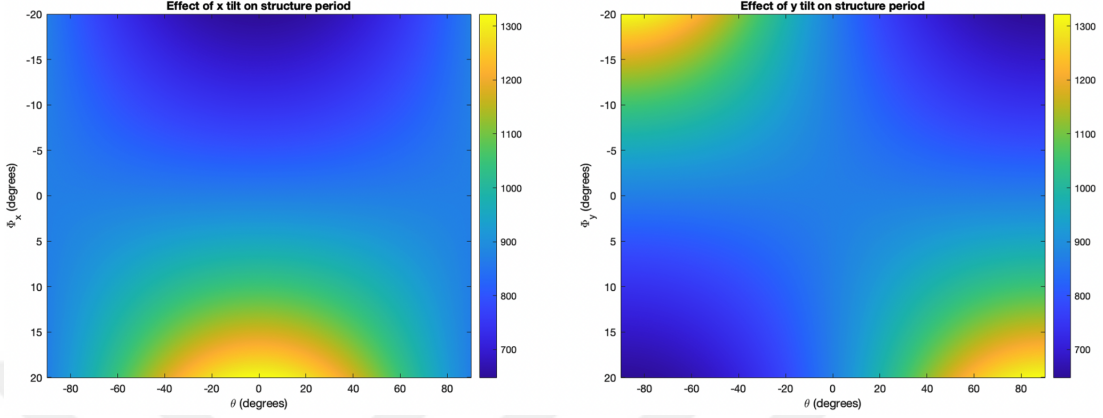


Figure 4.3: Behaviour of the structure period with changing tilt and observation angle. (Left) Plot of eq.4.34 considering tilt to be only along the x- direction. (Right) Plot of eq.4.34 considering tilt to be only along the y- direction.

Considering only the x-tilt, we see that the structure period is largest along the x-axis at a large tilt angle and also the smallest along the x-axis at large negative tilt angles. The effect of tilt decreases at larger polar angles. Note that, to perform a numerical experiment based on the plots above, we need to take into account the polarization of the beam as well. Thus we take the polarization angle to be the complement of the polar angle ($\theta = \beta + \frac{\pi}{2}$) to realize the above results experimentally. Having this picture in mind, the plot on the right makes sense since the light will be polarized along the x-axis for maximum effect of the y-tilt on the structure period and thus we obtain a plot that is essentially a shifted version of the plot on the left. Some of the numerical experiments with a fixed tilt value and varying polarization angles are given below.

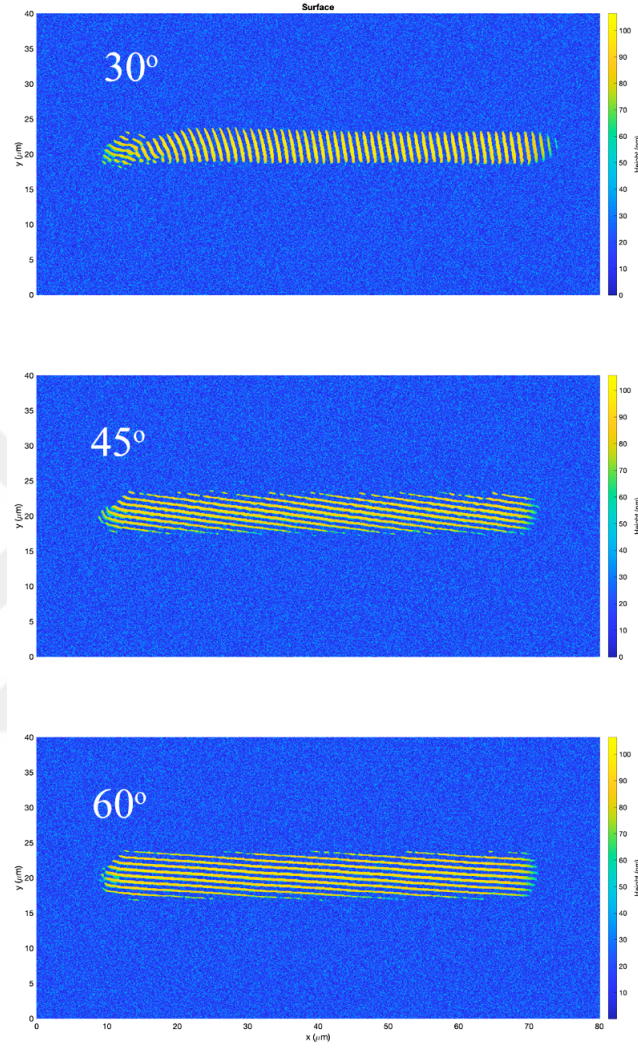


Figure 4.4: Simulations showing the effect of x-tilt on the NLL structures with varying polarization angles.

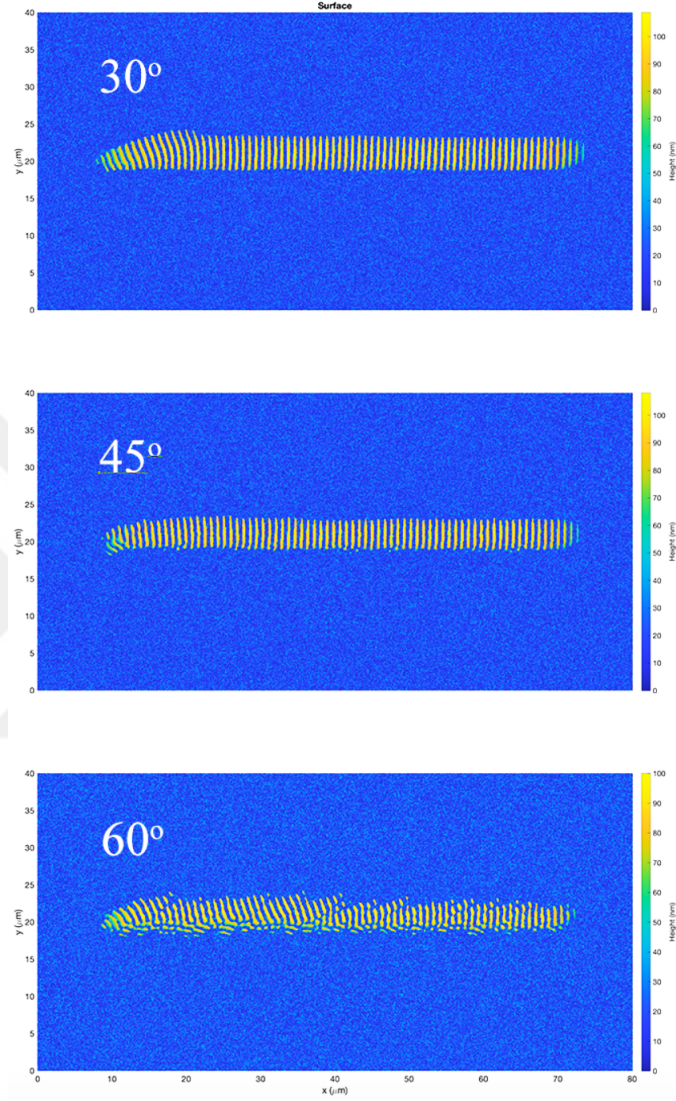


Figure 4.5: Simulations showing the effect of y-tilt on the NLL structures with varying polarization angles.

Using these numerical experiments, we can compare the period of the structures along the $\theta = \beta + \frac{\pi}{2}$ direction with those predicted by eq 4.34. The results comparing the effect of the x-tilt are shown below.

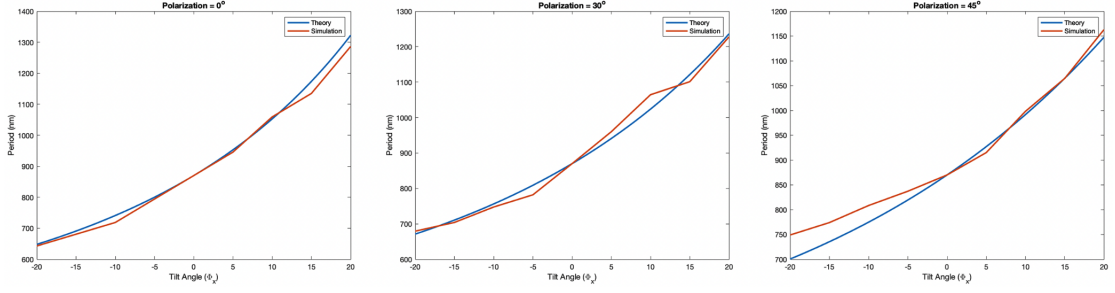


Figure 4.6: Comparison of the periods of NLL structures predicted by eq. 4.34 with those obtained by numerical simulations.

Eq. 4.34 also allows us to observe the effect of a coupled x-y tilt. Fixing θ , we can compare the effect of the x-y coupled tilt on the structure period. A plot for coupled x-y tilt at $\theta = 45^\circ$ is shown below.

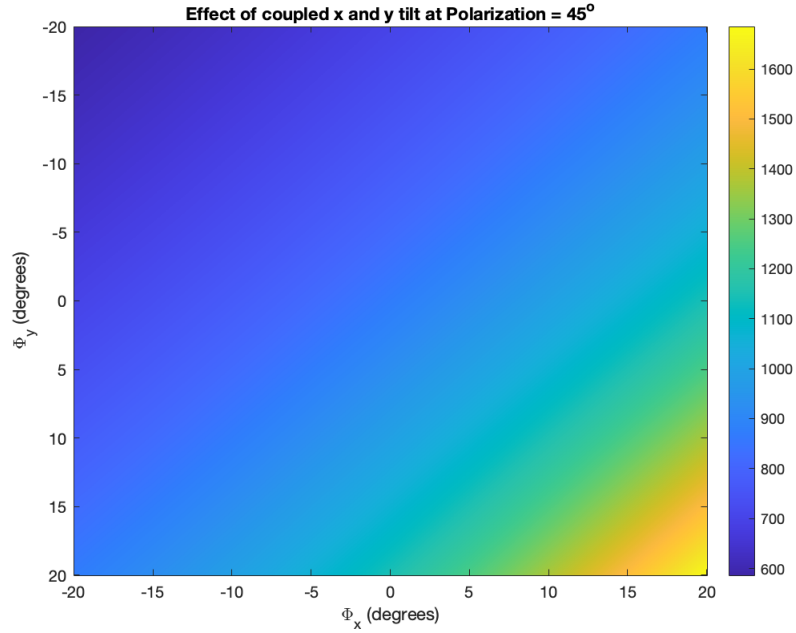


Figure 4.7: Behaviour of the structure period with coupled x-y tilt at 45° polarization.

Comparing the above plot with those in figure 4.1, we see that more extreme period values can be reached for the same tilt angles when the x-y tilt is coupled

compared to when they are separated from each other. The figure below shows some numerical experiments at $\theta = 45^\circ$ with different coupled tilt angles.

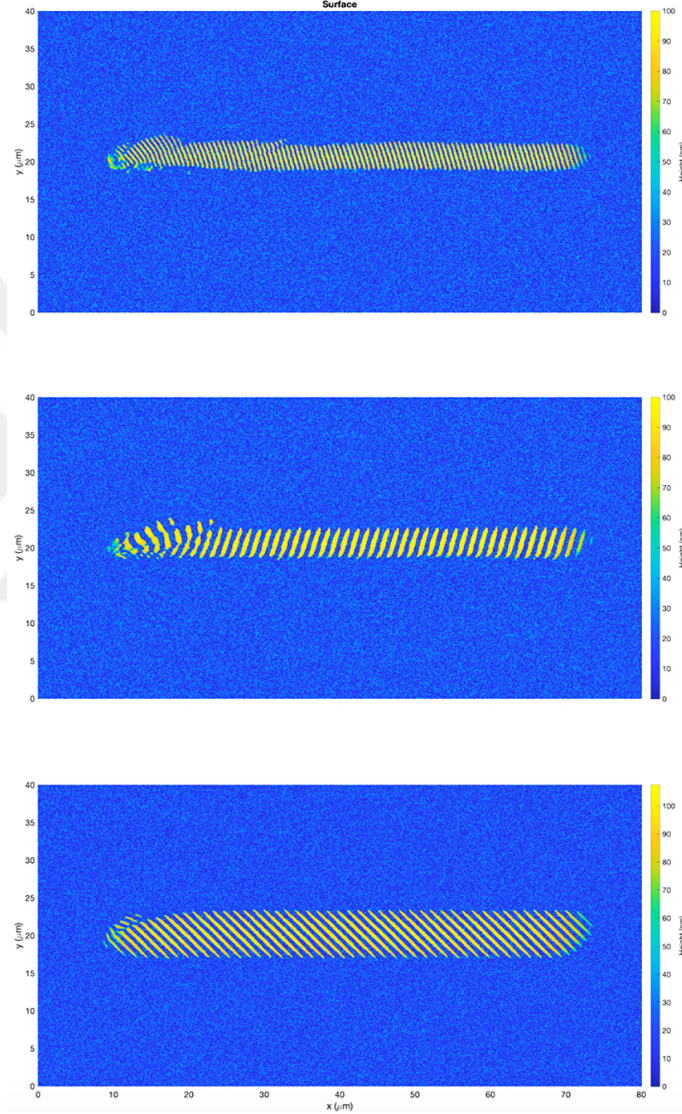


Figure 4.8: Simulations at 45° polarization with coupled x-y tilt. (Top) $\Phi_x = -20^\circ$ and $\Phi_y = -20^\circ$, (Center) $\Phi_x = 20^\circ$ and $\Phi_y = 20^\circ$, (Bottom) $\Phi_x = 20^\circ$ and $\Phi_y = -20^\circ$

Plotting the periods of the numerical experiments along with those predicted by eq 4.34, we get the following graphs.

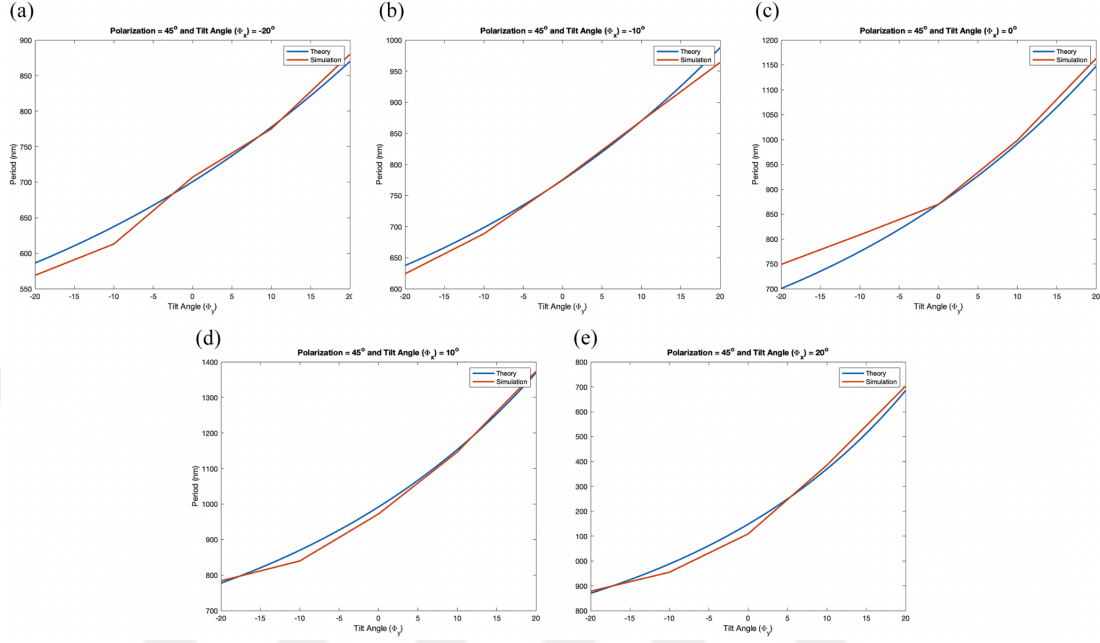


Figure 4.9: Comparison of the periods of NLL structures predicted by eq. 4.34 with those obtained by numerical simulations. The plots are obtained by fixing the polarization to 45° and the x-tilt to a particular value and plotting the period vs the y-tilt.

From the above plots shown in Fig. 4.9, a good match can be observed between theory and simulation. Thus, the model derived in eq. 4.34 seems to accurately predict the period of the structures formed due to the non-normal incidence of the laser beam on the material surface. However, the experimental validity of the model needs to be proved in future studies.

Chapter 5

Future prospects

During our investigations of Nonlinear Laser Lithography, we came across several interesting phenomena that can be pursued in future research, some of them are mentioned below.

5.1 A Third Type of NLL?

Earlier on in our studies of NLL on Silicon, we encountered another type of oxidation NLL which forms with almost the same parameters as the oxidation NLL mentioned earlier, with the only difference being the required average laser power. Furthermore, this oxidation NLL is perpendicular to the laser polarization causing one to speculate the possibility of the involvement of SPPs in its formation. The parameters mentioned in table 3.1 give oxidation NLL in Silicon parallel to the polarization. As the average power is decreased, one can observe perpendicular oxidation NLL structures beginning to emerge which take over below a certain intensity threshold.

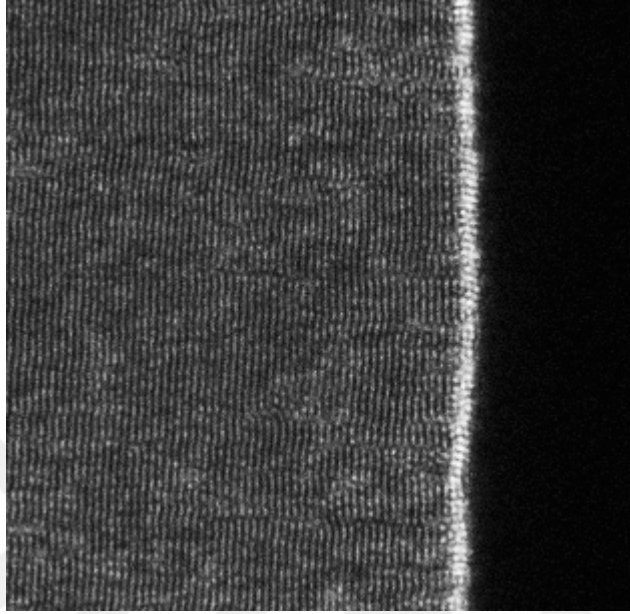


Figure 5.1: Microscope image showing the edge of a region on Silicon surface scanned by a laser beam. The left region shows Oxidation NLL formed perpendicular to the polarization, the bright boundary shows Oxidation NLL structures parallel to the polarization and the dark region is unprocessed Silicon.

The above figure shows a small region of Silicon processed with a horizontally polarized Laser beam to form oxidation NLL. The intensity is kept low so we observe the formation of the new oxidation NLL perpendicular to the Laser polarization. The bright edge is the region where we observe traditional oxidation NLL. The laser stops at the edge to change direction; causing this region to experience a higher average laser power that allows for the formation of parallel oxidation NLL. The SEM image of this perpendicular oxidation NLL is shown below.

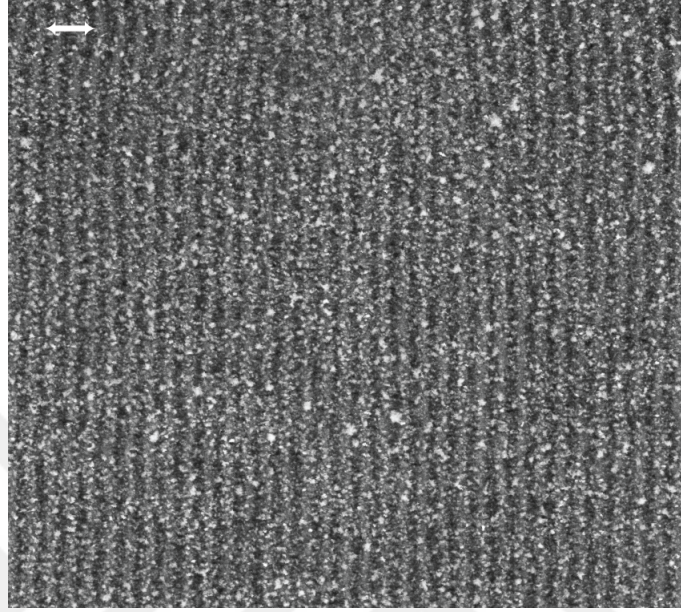


Figure 5.2: The third type of NLL (Oxidation NLL perpendicular to the laser polarization) as seen under SEM. The white arrow shows the laser polarization direction.

Similar but less vivid instances of perpendicular oxidation NLL were observed in the processing of Cobalt and Nickel samples. This thus offers a possibility of a detailed study of this third type of NLL which can lead to interesting new venues in LIPSS research.

5.2 Period Shift

While processing the Silicon sample for oxidation NLL, it was observed that the Silicon surface sometimes allows for the existence of NLL structures with different periods. The observation is shown in the microscope image below.

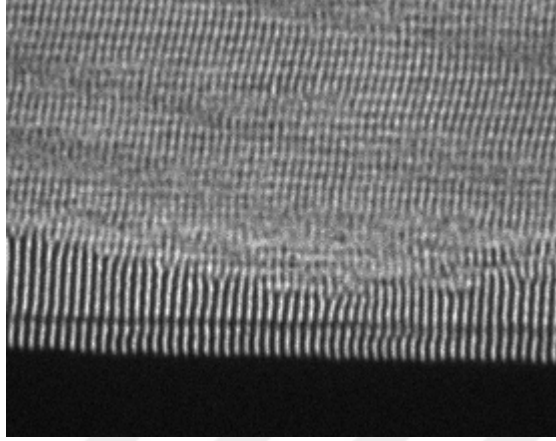


Figure 5.3: Period change observation in NLL on Silicon.

Initially, the structures with a larger period are observed. As the structure area grows, this larger period phase becomes unstable and new structures emerge that have a significantly shorter period. The interesting factor is the sudden shift in period rather than an adiabatic one, which causes one to think of this process as a first order phase transition. This change seems to occur quite randomly but can be due to the inhomogeneities in the surface roughness that act as defects. An argument in favor of this claim comes from the fact that this transition can be induced by introducing a defect. If we start scanning from a defective region, such as that burnt by high laser power, the structures that form when the laser emerges from this region have a shorter period.

This process is also observed in Oxidation NLL in Cobalt. The SEM image of this transition region in Cobalt is shown below.

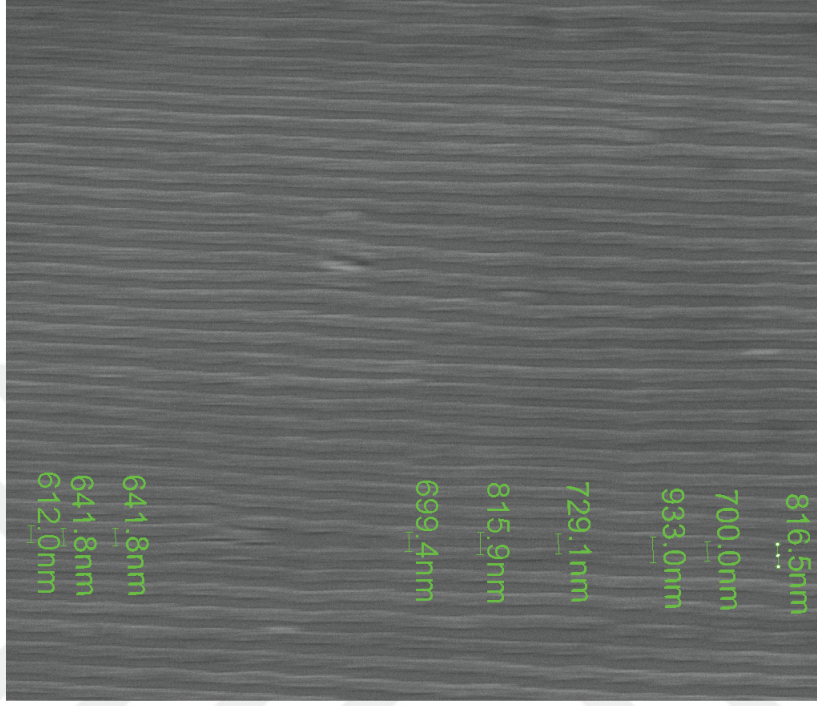


Figure 5.4: SEM image of the period change observation in NLL on Cobalt.

5.3 Vortex Beams with NLL

Bifurcations are ubiquitous in oxidation NLL. They can occur due to non-normal incidence of the laser beam and defects in the surface among other reasons. An example of a bifurcation is shown in Fig. 5.4. Similar to the possibility of using NLL for the formation of optical elements like diffraction gratings and Fresnel zone plates, it might be possible to use the bifurcations of NLL to form phase and amplitude masks allowing for the formation of optical vortices or vortex beams.

One easy way to generate a vortex beam is to use a fork grating [18]. A fork grating is a grating with a dislocation at the center as shown in Fig. 5.5(a). This kind of phase mask causes the cancellation of the electric field on the beam propagation axis. The beam thus circles the axis in the shape of a helical spiral. The following figure shows the fork grating required to form the vortex beam [19]

compared to that provided by NLL.

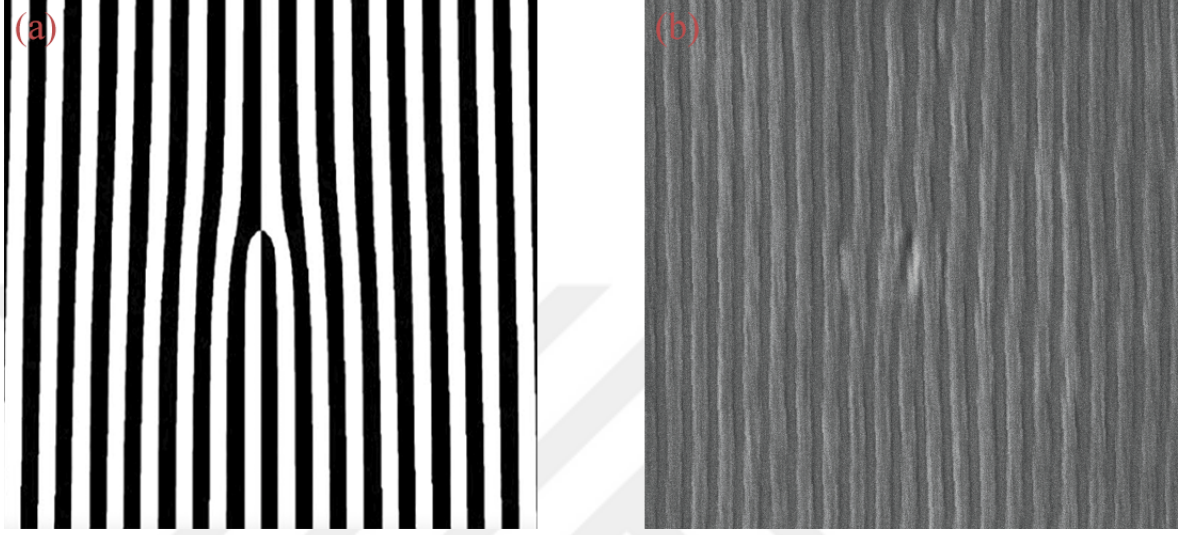


Figure 5.5: (a) The standard fork grating to obtain vortex beams (b) The fork grating provided by Oxidation NLL.

As shown in Fig. 5.5, the gratings in both cases seem to have a similar kind of dislocation. This thus hints at the possibility of using NLL for generating vortex beams.

5.4 Conformity of NLL Structures

Structure formation in NLL depends on feedback from the environment. New structures are formed based on the light scattered from older structures. The higher the structures, the stronger the feedback. These feedback mechanisms are the basis for the extreme regularity of NLL and its self-healing properties. Since the new structures are so dependent on the older ones, in a sense they conform to the influence of the older structures. But is there a limit to this conformity? Can the new structures escape the influence of the older ones, and if so, under what conditions? To provide some insight into some possible answers to these questions, a simple experiment is devised below.

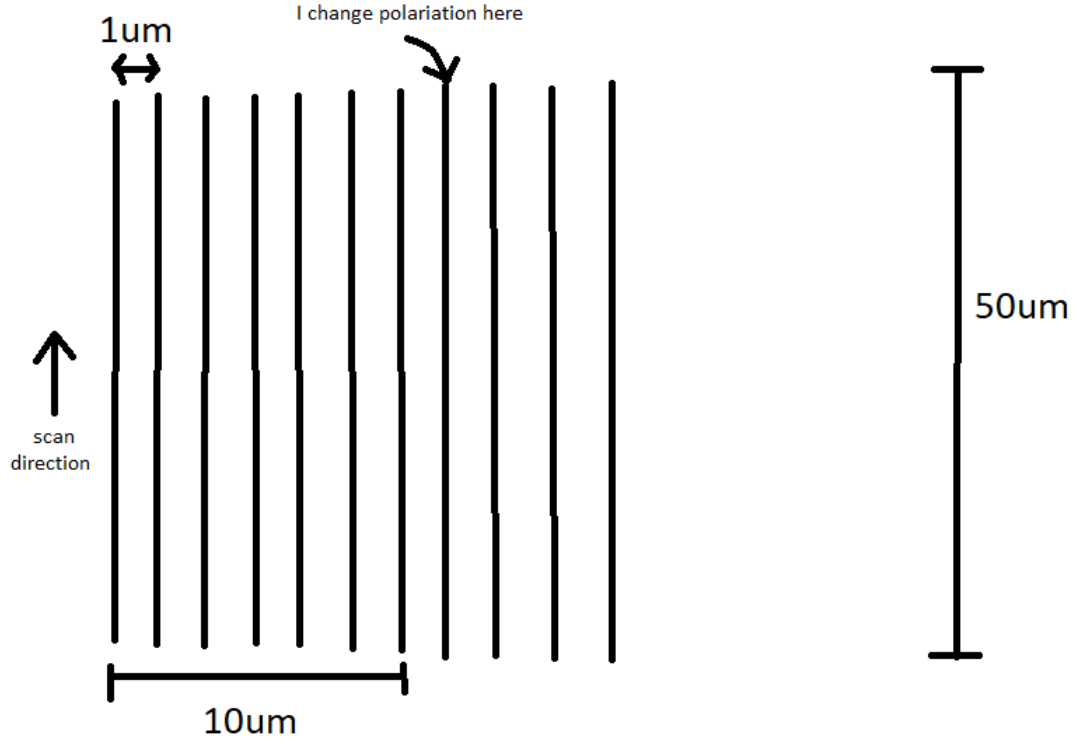


Figure 5.6: Schematic showing a sketch of an experiment to study the conformity of NLL. The beam is raster scanned on the sample and a large area is covered with structures, the polarization is then suddenly changed to see whether the structures conform to the feedback from the older structures or not.

As shown in the above figure, the Oxidation NLL structures are formed with a particular polarization and a large enough region is covered, by raster scanning the laser with a small step size, so that the new structures will receive significant feedback from the older structures. The total feedback is then strong since structures far away will also contribute a little to the feedback due to their scattered field. The laser is then moved to the edge of this region, the polarization is changed slightly ($\sim 1^\circ$) and the beam is raster scanned as normal. Without any feedback from the older structures, the new structures will be slightly tilted due to the change in polarization. But will the new structures tilt in the presence of feedback from the older structures, or will they conform to the feedback and

not change? And if they conform, what is the threshold change in polarization at which they will stop conforming? The experimental setup mentioned above might be able to provide some answers to these questions.



Chapter 6

Conclusion

In this thesis we explored the spatial and temporal symmetry breaking in NLL. The spatial symmetry is broken from an infinite-fold rotational symmetry to a 2-fold rotational symmetry. This symmetry breaking occurs due to two processes, Oxidation NLL structures formed at high-intensity regions caused by the interference between incident and scattered electric fields, and Ablation NLL structures formed due to the interference between the incoming E-field and SPPs. We discussed some techniques using which the two NLL processes can be obtained on the same surface. We also explored the phase space and found regions where the Oxidation and Ablation NLL structures reside. Furthermore, we investigated the versatility of the two NLL processes by obtaining them on different materials.

We saw that tilting the laser beam towards or away from the scanning direction leads to temporal symmetry breaking. If the beam is scanned such that the tilt direction is along the scanning direction, then the period of the structures becomes smaller while it increases if the beam is scanned in the opposite direction. This allowed us to observe a type of solid-state Doppler effect.

These spatial and temporal symmetry breakings can have interesting applications, as shown in chapter 3. Lastly, we saw that the techniques developed in this research open up new areas of research related to the field of LIPSS.

Bibliography

- [1] C. Kerse, H. Kalaycıoğlu, P. Elahi, B. Çetin, D. K. Kesim, Ö. Akçaalan, S. Yavaş, M. D. Aşık, B. Öktem, H. Hoogland, *et al.*, “Ablation-cooled material removal with ultrafast bursts of pulses,” *Nature*, vol. 537, no. 7618, pp. 84–88, 2016.
- [2] H. Lubatschowski, “Ultrafast lasers in ophthalmology,” *Physics Procedia*, vol. 5, pp. 637–640, 2010. Laser Assisted Net Shape Engineering 6, Proceedings of the LANE 2010, Part 2.
- [3] H. Lubatschowski, A. Heisterkamp, F. Will, A. I. Singh, J. Serbin, A. Ostendorf, O. Kermani, R. Heermann, H. Welling, and W. Ertmer, “Medical applications for ultrafast laser pulses,” *Riken Review*, pp. 113–118, 2003.
- [4] S. Backus, C. G. Durfee III, M. M. Murnane, and H. C. Kapteyn, “High power ultrafast lasers,” *Review of scientific instruments*, vol. 69, no. 3, pp. 1207–1223, 1998.
- [5] K. Sugioka and Y. Cheng, “Ultrafast lasers—reliable tools for advanced materials processing,” *Light: Science & Applications*, vol. 3, no. 4, pp. e149–e149, 2014.
- [6] M. Birnbaum, “Semiconductor surface damage produced by ruby lasers,” *Journal of Applied Physics*, vol. 36, no. 11, pp. 3688–3689, 1965.
- [7] J. Bonse, J. Krüger, S. Höhm, and A. Rosenfeld, “Femtosecond laser-induced periodic surface structures,” *Journal of Laser Applications*, vol. 24, no. 4, p. 042006, 2012.

- [8] F. Keilmann and Y. Bai, “Periodic surface structures frozen into co2 laser-melted quartz,” *Applied Physics A*, vol. 29, no. 1, pp. 9–18, 1982.
- [9] H. U. Lim, J. Kang, C. Guo, and T. Y. Hwang, “Manipulation of multiple periodic surface structures on metals induced by femtosecond lasers,” *Applied Surface Science*, vol. 454, pp. 327–333, 2018.
- [10] J. Sipe, J. F. Young, J. Preston, and H. Van Driel, “Laser-induced periodic surface structure. i. theory,” *Physical Review B*, vol. 27, no. 2, p. 1141, 1983.
- [11] Z. Guosheng, P. Fauchet, and A. Siegman, “Growth of spontaneous periodic surface structures on solids during laser illumination,” *Physical Review B*, vol. 26, no. 10, p. 5366, 1982.
- [12] A. M. Bonch-Bruевич, M. N. Libenson, V. S. Makin, and V. V. Trubaev, “Surface electromagnetic waves in optics,” *Optical Engineering*, vol. 31, no. 4, pp. 718–730, 1992.
- [13] J. F. Young, J. Sipe, J. Preston, and H. Van Driel, “Laser-induced periodic surface damage and radiation remnants,” *Applied Physics Letters*, vol. 41, no. 3, pp. 261–264, 1982.
- [14] B. Öktem, I. Pavlov, S. Ilday, H. Kalaycıoğlu, A. Rybak, S. Yavaş, M. Erdoğan, and F. Ö. Ilday, “Nonlinear laser lithography for indefinitely large-area nanostructuring with femtosecond pulses,” *Nature photonics*, vol. 7, no. 11, pp. 897–901, 2013.
- [15] J. Bonse, S. Höhm, S. V. Kirner, A. Rosenfeld, and J. Krüger, “Laser-induced periodic surface structures—a scientific evergreen,” *IEEE Journal of selected topics in quantum electronics*, vol. 23, no. 3, 2016.
- [16] Q. Sun, F. Liang, R. Vallée, and S. L. Chin, “Nanograting formation on the surface of silica glass by scanning focused femtosecond laser pulses,” *Optics letters*, vol. 33, no. 22, pp. 2713–2715, 2008.
- [17] Ö. Yavuz, *Controlled Surface Structuring with Nonlinear Laser Lithography*. PhD thesis, Bilkent Universitesi (Turkey), 2018.

- [18] Y. Zhuang, Q. Yang, P. Wu, W. Zhang, Y. Ren, and H. Liu, “Vortex beam array generated by a volume compound fork grating in lithium niobite,” *Results in Physics*, vol. 24, p. 104083, 2021.
- [19] P. Soleimani, H. Khoshima, and M. Yeganeh, “Optical vortex beam controlling based on fork grating stored in a dye-doped liquid crystal cell,” *Scientific Reports*, vol. 12, no. 1, p. 21271, 2022.

