Formation mechanisms of femtosecond laser-induced periodic surface structures on Silicon

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Outline

1. Introduction
   - Applications of surface microstructures
   - Formation mechanisms of ripples
2. Modeling of the interaction
3. Results
   - Conditions on dielectric constants
   - Conditions on the phase-matching
   - Resulting periodicities
4. Conclusions

Outline

Typical microstructure formation after fs laser pulses

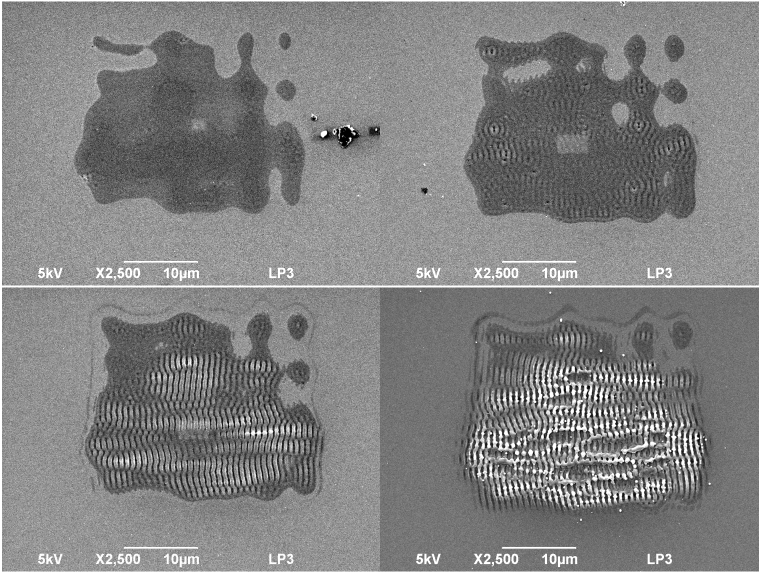


Figure: Femtosecond laser interaction on a silicon target [Torres, 2011].

Typical microstructure formation after fs laser pulses

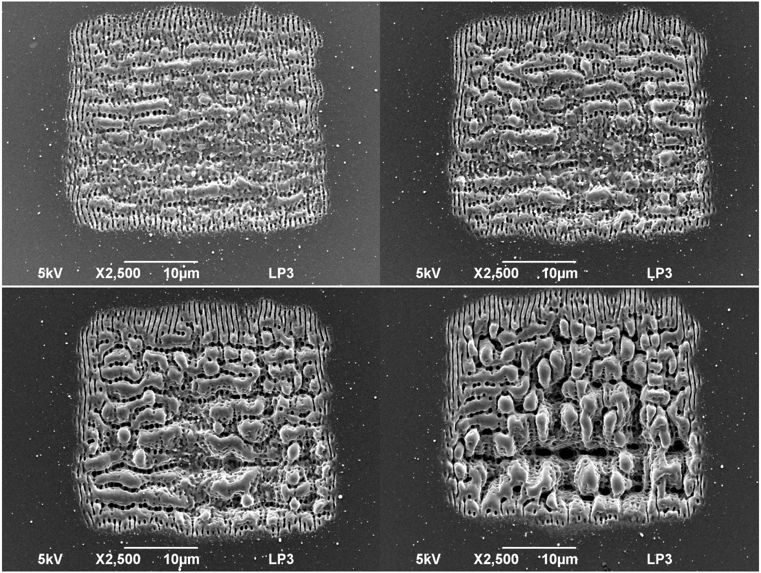


Figure: Femtosecond laser interaction on a silicon target [Torres, 2011].

Application of rippled structures

- Colorizing metals [Vorobyev and Guo, 2008],
- laser marking [Dusser et al., 2010],
- grating production : ripples reach 50 nm today in metals [Afshar et al., 2012]

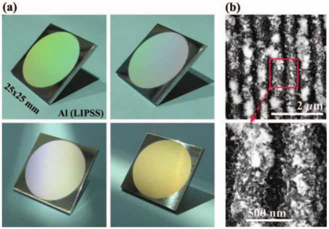


FIG. 3. (Color) Color aluminum due to femtosecond laser-induced NC LIPSSs. (a) Photographs show that the same Al sample exhibits various colors depending on the viewing angle. (b) SEM images showing NC LIPSSs on the color aluminum sample in (a).

FIGURE: ”Colorized metals” [Vorobyev and Guo, 2008].

Applications of conical structures

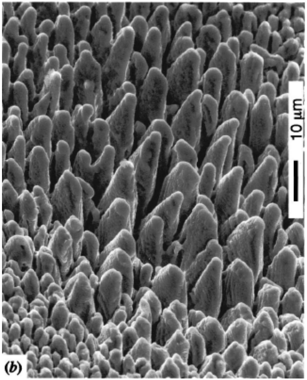
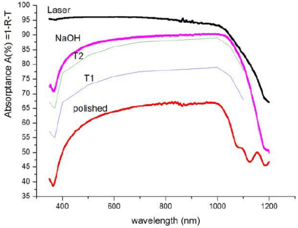


FIGURE: "Black Silicon" formed after ~100 irradiations by femtosecond laser.

- Solar-cells with enhanced absorption [Torres, 2011, Sarnet et al., 2008]



- pH-meter, cell substrate [Ranella et al., 2010]
- Custom wetting properties [Zorba et al., 2007]
- THz wave generation [Hoyer et al., 2008]

Motivation

With the use of femtosecond laser :

- it became possible to produce sub-wavelength structures
- it became possible to make structures on dielectrics

Why ?

More understanding of the physical mechanisms is required to improve the control, efficiency, and outpass the limits.

Outline

Formation mechanisms of rippled microstructures

Many models have been proposed since Birnbaum [1965].

- Electromagnetic models
  - Scattering on roughness ("Sipe model") [Sipe et al., 1983]
  - Surface plasmon polariton (SPP) excitation [Emel'yanov et al., 1989, Huang et al., 2009]
- Non-resonant models
  - Capillary wave excitation [Ursu et al., 1985]
  - Defect accumulation [Emel'yanov and Soumbatov, 1996, Emel'yanov, 2009]

However

It is not well-known if femtosecond laser irradiation leads to :
- substantial surface melting ?
- surface electromagnetic wave excitation ?

Types of microstructures

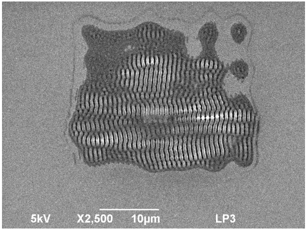


FIGURE: Ripples formed after $N = 3$, $\lambda = 800$ nm, $\tau = 100$ fs laser pulses.

Structures can be separated into two categories [Prokhorov et al., 1990] :

- *Resonant* structures : correlated with laser wavelength $\Lambda \sim \lambda$, polarization dependent
- *Non-resonant* structures : correlated with melted depth $\Lambda \sim f(h)$

Focus

In this talk, we focus on the resonant ”LSFL” structures e.g. $\Lambda \sim \lambda$, linked to laser polarization.

What do we propose ?

- We developped a 2D simulation code in order to test the surface wave period modification and to calculate the thermal consequences of ONE femtosecond pulse.

We identify the laser parameters leading to :

- satisfy the conditions for surface wave generation on Si,
- the melting of the surface, and obtained melted depth

In this talk, the following questions are considered :

- Can Surface Plasmon Polariton excitation lead to the ripple formation ?
- If yes, with which parameters ?
- Which type of ripple do they explain ?
- What are the differences with roughness "Sipe" model ?
- Is it possible to excite SPP with a single laser pulse ?

Involved processes

- Absorption by the free-carriers
- One-photon and two-photon ionization, impact ionization
- Diffusive transport of the free-carriers, diffusion of lattice energy.
- Layered surface reflectivity
- Free-carrier heating
- Auger recombination
- Surface thermo-emission of carriers

Timescales of processes

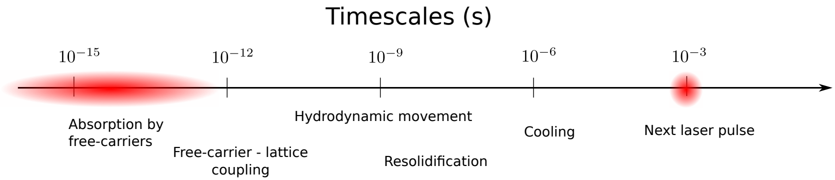


FIGURE: Caracteristic timescale in the femtosecond laser interaction with semi-conductors.

Optical Absorption

Hyp : System can be considered as a dense plasma since excitation of free-carriers (conduction band electrons) lead to a large density *[Sokolowski-Tinten and von der Linde, 2000]*

Hyp2 : electrons and lattice are thermodynamically coupled. Each is considered at local thermodynamic equilibrium *[Anisimov et al., 1974]*.

- Dielectric function is described using Drude model in a solid

$$\varepsilon_{Si}(\omega, n_e, \nu) = 1 + (\varepsilon_\infty(\omega) - 1)\frac{n_0 - n_e}{n_0} - \frac{\omega_p^2}{\omega^2\left(1 + i\frac{\nu_{coll}}{\omega}\right)}$$

where $\omega_p^2 = \frac{n_e e^2}{m^\star \varepsilon_0}$, and $m^{\star -1} = m_e^{-1} + m_h^{-1}$.

- Absorption takes into account free-carrier absorption, one & two-photon transitions.

$$\frac{\partial I}{\partial z} = -\alpha_{fcr} I - (\sigma_1 I + \sigma_2 I^2)\frac{n_0 - n_e}{n_0} \tag{1}$$

with $\alpha_{fcr} = \frac{2\omega}{c} Im\sqrt{1 - \frac{\omega_p^2}{\omega^2}\frac{1}{1+i\frac{\nu}{\omega}}}$ (see **??**).

Surface reflectivity is taken into account by

$$R_{i,k} = \left|\frac{r_{i,i+1} + r_{i+1,k}e^{-2i\phi_{i+1}}}{1 + r_{i,i+1}r_{i+1,k}e^{-2i\phi_{i+1}}}\right|^2$$

Free-carrier transport

- Free-carrier balance is calculated

$$\frac{\partial n_e}{\partial t} + \nabla . \boldsymbol{J_e} = G_e - R_e \tag{2}$$
$$\boldsymbol{J_e} = -k_B T_e \mu_e \nabla n_e$$
$$G_g = \left[\frac{\sigma_1 I}{\hbar\omega} + \frac{\sigma_2 I^2}{2\hbar\omega} + \delta_I n_e \right] \frac{n_0 - n_e}{n_0}$$
$$R_e = \frac{n_e}{\tau_0 + \frac{1}{C n_e^2}}$$

The free-carrier mobility is taken as $\mu_e = \frac{e}{m^\star \nu_{coll}}$

- Thermo-emission at the surface

$$-D_e \left. \frac{\partial n_e}{\partial z} \right|_{z=0} = \frac{J_{th}}{e}$$

$$J_{th} = A \left. T_e^2 \right|_{z=0} e^{-\frac{\psi}{k_B T_e}}, \; A = \frac{4\pi m_e k_B^2 e}{h^3}, \; \psi = 4.6 \text{ eV}.$$

Energy transport and relaxation

- Free-carrier energy

$$\frac{1}{4\nu_{coll}}\frac{\partial^2 T_e}{\partial t^2}+\frac{\partial T_e}{\partial t}=\nabla\left(D_{SBD}\nabla T_e\right)-\frac{\gamma_{ei}}{C_e}\left(T_e-T_{Si}\right)+\frac{Q_e}{C_e}$$

$$Q_e=\left[\left(\hbar\omega-E_g\right)\frac{\sigma_1 I}{\hbar\omega}+\left(2\hbar\omega-E_g\right)\frac{\sigma_2 I^2}{2\hbar\omega}-E_g\delta_I n_e\right]\frac{n_0-n_e}{n_0}$$
$$+\alpha_{IB}I+E_g R_e-\frac{3}{2}k_B T_e\frac{\partial n_e}{\partial t}$$

- Lattice energy

$$C_{Si}\frac{\partial T_{Si}}{\partial t}=\nabla\left(\kappa_{Si}\nabla T_{Si}\right)+\gamma_{ei}\left(T_e-T_{Si}\right)$$

- Coupling

$$\gamma=\frac{C_e}{\tau_\gamma}=\frac{3}{2}k_B n_e\left[\tau_{\gamma 0}\left(1+\frac{n_e}{n_{th}}\right)^2\right]^{-1} \qquad (3)$$

Electronic pressure effects

- Modification of the band structure under high electronic pressure

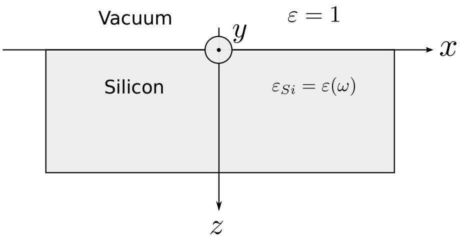
$$E_g(T, n_e) = 1.17 - 4.73\,10^{-4}\frac{T^2}{T+636} - 1.5\,10^{-10} n_e^{1/3}$$

- Melting temperature also changes with free-carrier density [Combescot and Bok, 1985]

$$T_m = T_m^0 - \frac{n_e E_{gap}}{\rho_{Si} c_l} \tag{4}$$

Outline

Conditions on the dielectric function



1. Continuity of the electric field : requirement of a metal-dielectric interface

$$\Re e\,(\varepsilon_1)\,\Re e\,(\varepsilon_2) < 0$$

2. Continuity of the magnetic field leads to the condition

$$\Re e\,(\varepsilon_2) < -\Re e\,(\varepsilon_1)$$

Raether [1986], Zayats et al. [2005], Maier [2007]

Excitation of an "active" layer

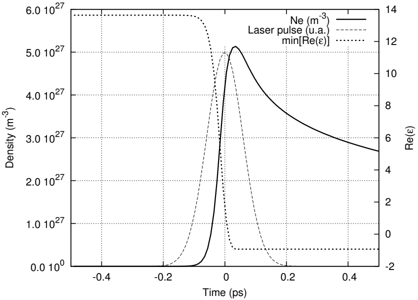


FIGURE: Evolution of free-carrier plasma during 0.5 $J.cm^{-2}$, $\tau = 100$ fs, $\lambda = 800$ nm laser pulse.

Description

The amount of free-carriers is dramatically increased from $10^{16}\ m^{-3}$ to $> 10^{27}\ m^{-3}$ in few tens of fs.

Absorption becomes metallic during the irradiation. Critical density is slightly exceeded.

$n_{cr} = \frac{m_e \varepsilon_0 \varepsilon_\infty \omega^2}{e^2} \sim 4.6\ 10^{27}\ m^{-3}$.

Above critical density, absorption is cut, but excited electrons ionize more electrons by avalanche.

Excitation parameters

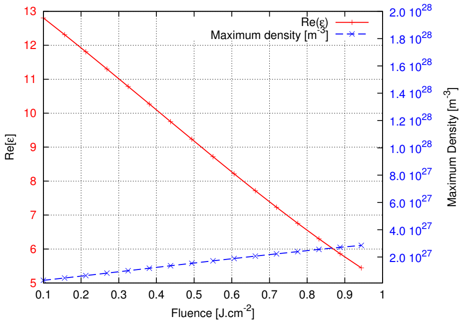


FIGURE: $\tau = 500\ fs$, $\lambda = 800$ nm.

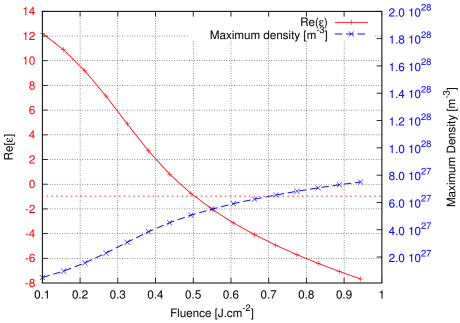


FIGURE: $\tau = 50$ fs.

Conclusion

SPP can be excited at the Si surface during the femtosecond laser pulse at high intensity ($10^{13}\ W.cm^{-2}$).

SPP excitation range

Generalization with $\lambda = 800$ nm can be given as a function of laser intensity.

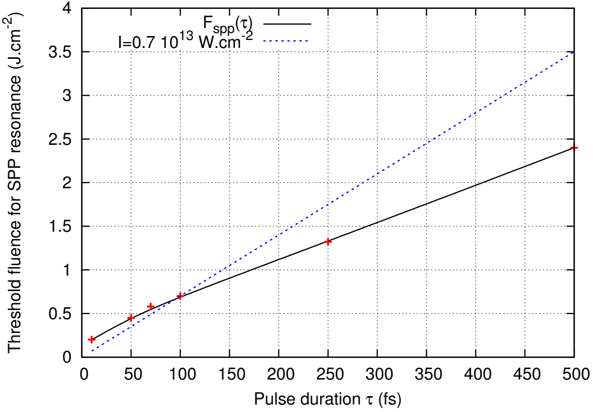


FIGURE: Threshold intensity for SPP excitation

Outline

Coupling devices

- SPP cannot be excited on a flat surface since laser dispersion curve does NOT meet the surface plasmon dispersion curve. A coupling device is necessary.

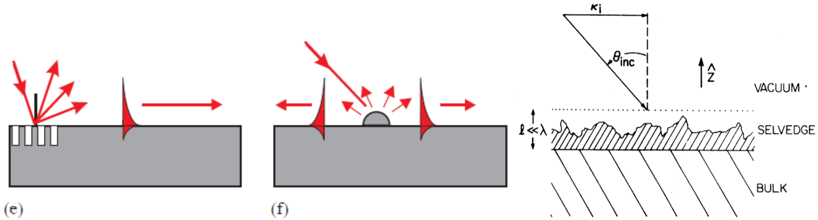


FIGURE: *Scattering configurations leading to SPP excitation*. (e) scattering on gratings, (f) scattering by a defect [Zayats et al., 2005], (g) Scattering by surface roughness [Sipe et al., 1983, Maier, 2007]

Scattering configurations

- Gratings : On metals, Garrelie et al. [2011] well demonstrated that ripples are only formed while grating period is the SPP one.
- Scattering on roughness :
  - Which minimal roughness amplitude is needed for the scattering ?
  - What is the link with SPP ?
- Was scattering by nanoparticle / defect observed ?

Scattering by a defect : $d \sim \lambda$, $N = 1$

$\lambda = 800$ nm, $\tau \sim 100$ fs.

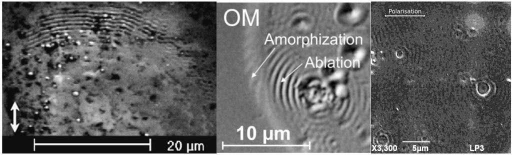


FIGURE: Scattering on defects (a) Guillermin and Sanner [2007], (b) Bonse et al. [2009], (c) Derrien et al. [2012]

Scattering on defects

- Observed by several groups.
- Explained by Localized Surface Plasmon (LSP) excitation (still require $\Re e\,(\varepsilon) < -1$)
- Leads to periodic modulation of the surface with ONE pulse (but not to *parallel* ripples).

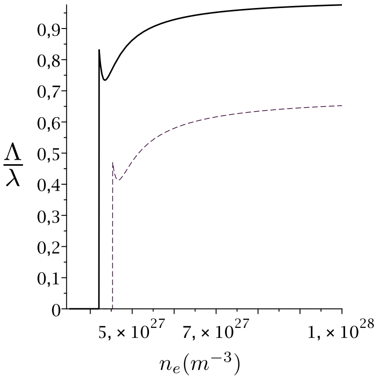
SPP coupling by roughness

But ... what is the link between Sipe theory and SPP ?

- The SPP excitation by surface roughness scattering is included in the classical "Sipe" theory. However, scattering on $d \sim \lambda$ defects is not included.
- We identified the laser parameters leading to excite *one* type of surface waves : the Surface Plasmon Polaritons.
- We calculated the duration and thickness of the active layer.
- We reviewed the methods to satisfy the phase-matching conditions and showed SPP are excited by scattering with a defect ($\delta \sim \lambda$) or by scattering with surface roughness ($\lambda \gg \delta > 7$ nm).

Outline

Surface plasmon polariton period



$$\Lambda = \frac{\lambda}{\left(\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^{1/2} \pm \sin\theta}$$

FIGURE: Wavelength normalized period of SPP as a function of free-carrier density, while conditions of resonance at Air - Si interface (thick line) and $SiO_2 - Si$ interface (dashed line) are met.

Period of surface waves with roughness

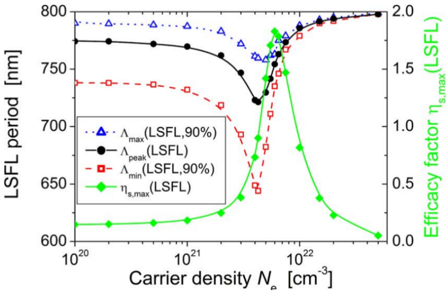


FIGURE: Period of the roughness-scattered waves as a function of density (Courtesy of Bonse et al. [2009]).

- In the case of femtosecond interaction, Bonse et al. [2009] gave the modification of the period as a function of free-carrier density $\Lambda(n_e)$.
- However, *density is space-time-dependent* $n_e = n_e(t, \mathbf{r})$
- Measured period depends on averaging processes such as free-carrier - lattice thermal coupling, and free-carrier thermal diffusion.
- The roughness-diffracted wave has been introduced in the simulations. Thus the evolution of the excited wave period is calculated.

The role of free-carrier transport

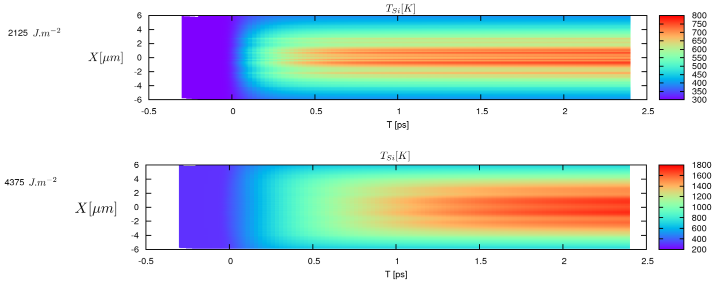


FIGURE: Evolution of surface lattice temperature profiles. $\tau = 100$ fs. $\lambda = 800$ nm.

Diffusive transport

Increasing laser fluence leads to smooth the smallest spatial frequencies excited by scattering on roughness. This mechanism contributes to increase of the observed period with laser fluence.

Periodicity with laser fluence

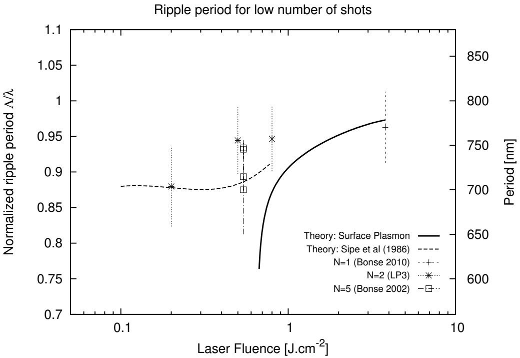


Figure: Experimental measurements of the LSFL periods obtained at LP3 laboratory, as a function of laser fluence. $\tau = 100$ fs, $\lambda = 800$ nm, $\theta = 0°$. The periods resulting from theoretical investigations are also represented.

Role of laser fluence (low N)

Increasing laser fluence increases the structure periodicity.
- Low F, $N > 1$: scattering on roughness.
- High F, $N = 1$: scattering on defects.

Conclusions

Mechanisms

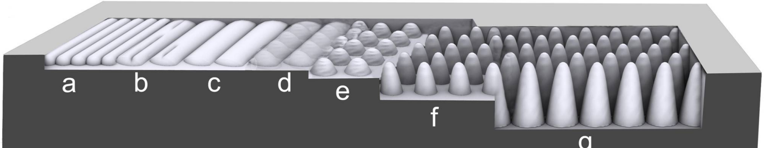
- Surface-Plasmon-Polaritons are excited on Si under intense laser irradiation. The laser parameters to excite the SPP on Si have been identified.
- The presence of a surface defect or of a $\gtrsim$ 5 nm roughness is necessary for the ripple formation.
- The classical model well explains the formation mechanisms of the LSFL ripples under femtosecond laser pulse. The "Sipe-Drude" model explaining subwavelength structures is confirmed. Cases of single pulse surface waves is due Localized Surface Plasmon excitation, by scattering on nanoparticles.

Control

- In femtosecond interaction, the angle of incidence is not important to excite SPP, but is important for the control of the period.
- Increasing laser fluence lead to enhance thermal diffusion, which contributes to smooth the highest spatial frequencies.

Future works

- Other types of surface waves exist at lower fluences, and may not require the optical activation [Driel, 1982, Sipe, 1985]. The large density gradient may also lead to non-linear optical effects and can explain other types of small surface structures.
- Explain the HSFL ripples, explain large ripple formation, explain bead formation... !
- Investigate cumulative effects : defect incubation, irradiation of structured surfaces, ...
- A global approach is required to explain the large variety of observed microstructures and to improve their control.
    - Couple Maxwell 3D + material excitation to explain the resonant processes and investigate types of surface waves ($\sim$ 100 nm structures for grating production and microfluidic channels).
    - Couple material absorption + Navier-Stokes 3D to explain non-resonant structures (structures for photovoltaics and wetting modfication).



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