The efficacy of plasmonic model to calculate HSFL nanostructure period in Sapphire

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Abstract. In this work, we try to determine all the period of nanostructure subwavelength that can be observed during irradiation by multipulse femtosecond laser in dielectric materials. For this, we use a generalized plasmonic model developed previously to follow the evolution of the periods of the nanostructures on the Sapphire material and their optical properties according to electron-holes plasma excitation and varying the optical spectrum between 300 and 1400 nm. We find a nanostructure area where all the period observed experimentally must be included inside it. This plasmonic model shows its efficiency and its precision on a nanoscale.

1. Introduction
Laser induced periodic surface structures (LIPSS) became a phenomenon worthy of research and study due to its effectiveness in increasing the profitability of optical absorption and in general enhance the surface performance of materials, which will make huge progress in the world of technology such as micro solar cells devices [1, 2, 3]. LIPSS appear in general in all material during the irradiation by ultrashort laser pulse [4]. There are two kinds of LIPSS but the most important is the so called high spatial frequency LIPSS (HSFL). However, if we look in depth at literature, we will find out that the origin of the formation of this type of LIPSS is not yet well understood, where many explanation has been proposed such as interference model [5, 6] second harmonic generation (SHG) [7, 8], surface plasmon polariton excitation [9, 10] and recently, a new hypothesis has been proposed in our previous work [11] which considers that the plasmon excitation effect for non-thermal melting dynamics (disorder) can be considered as a fundamental process for periodic of nanoablation as the origin of HSFL nanostructures.

In this paper, by considering the plasmonic excitation as the mechanism responsible of the periodicity of the nanostructures, we will try to calculate based on our generalized plasmonic model proposed in [11] all the periods of nanostructures which can be formed at the surface of Sapphire material by browsing the wavelengths spectrum in the range of 300 to 1400 nm of the femtosecond (fs) laser wavelength.
2. Theoretical Model

Miyaji et al [12] proved experimentally that a metal-like film which called here pseudo-metal layer is induced at the surface of dielectric materials during the irradiation by multipulse fs-laser. For this reason, a generalized plasmonic model is used to study the development of periodical nanostructures on Sapphire surface during the irradiation with multipulse femtosecond laser at wavelengths between 300 and 1400 nm. The air is considered as the dielectric environment. The SPP dispersion relation is [13]:

$$\omega^2 = c^2 k_{sp}^2 \frac{\varepsilon_{pm} + \varepsilon_d}{\varepsilon_{pm}\varepsilon_d}.$$  (1)

where $\varepsilon_{pm}$ is the dielectric function of pseudo-metal layer and $k_{sp} = k_{sp1} + ik_{sp2}$ is the plasmon propagation number with $k_{sp1} = \Re k_{sp} = \frac{2\pi}{\lambda_{sp}} = \frac{\pi}{\Lambda}$ ([14]) where $\lambda_{sp}$ is the plasmon wavelength and $\Lambda$ is the period of nanostructures and $\varepsilon_d$ is the dielectric function of the material surrounding the pseudo-metal layer. This dielectric function is considered as $\varepsilon_d = m\varepsilon_{sa} + (1 - m)\varepsilon_{air}$ where $m$ represents the factor of mixed state depending implicitly on the pulse number and it varies from 0 and 1, $\varepsilon_{air} = 1$ and $\varepsilon_{sa}$ depend laser wavelengths according to the relationship

$$n^2 - 1 = \frac{1.4313493\lambda^2}{\lambda^2-0.0726631^2} + \frac{0.65054713\lambda^2}{\lambda^2-0.1193242^2} + \frac{5.3414021\lambda^2}{\lambda^2-18.028521^2}$$ (\lambda \text{ in nm}) with $\varepsilon_{sa} = n^2$ ([15]). The dielectric function of the pseudo-metal layer is given by the Drude model [16]:

$$\varepsilon_{pm} = \varepsilon_{pm1} + i\varepsilon_{pm2} = 1 + (\varepsilon_{sa} - 1)(1 - \frac{n_{eh}}{n_0}) - \frac{\omega_p^2}{\omega^2} \frac{1}{1 + \frac{1}{\omega^2\tau_{ee}}},$$  (2)

with

$$\varepsilon_{pm1} = 1 + (\varepsilon_{sa} - 1)(1 - \frac{n_{eh}}{n_0}) - \frac{\omega_p^2}{\omega^2} \frac{1}{1 + \frac{1}{\omega^2\tau_{ee}}},$$  (3)

$$\varepsilon_{pm2} = \frac{1}{\omega\tau_{ee}} \frac{\omega_p^2}{\omega^2} \frac{1}{1 + \frac{1}{\omega^2\tau_{ee}}},$$  (4)

where $n_0$ is the electron concentration in the valence band (we consider a value of $10^{23}$ cm$^{-3}$), $\tau_{ee}$ the electron-electron collision time (1 fs), $\omega$ is laser frequency and $\omega_p = \frac{n_{eh}e^2}{\varepsilon_0 m_{opt}^* m_e}$ is plasma frequency, with $m_{opt}^* = 0.3$ [17] for Sapphire material.

Through the combination of Eq.1 and Eq.2, we found the following generalized plasmonic model:

$$k_{sp1} = \frac{1}{\sqrt{2} c} \sqrt{\frac{\gamma\alpha}{(\alpha^2 + \beta^2)} + \frac{\gamma}{(\alpha^2 + \beta^2)} \frac{1}{2}},$$  (5)

$$k_{sp2} = \frac{\omega^2}{2c^2 k_{sp1} (\alpha^2 + \beta^2)}. $$  (6)

Where, $\alpha = \varepsilon_{pm1}^2 + \varepsilon_{pm2}^2 + \varepsilon_d \varepsilon_{pm1}$, $\beta = \varepsilon_d \varepsilon_{pm2}$ and $\gamma = \varepsilon_d (\varepsilon_{pm1} + \varepsilon_{pm2})$.

For more details see Ref.[11]. This model was simulated using MATLAB software.
3. Results and Discussion

The excitation of dielectric material surface such as Sapphire by multipulse femtosecond laser at low fluence can induce a pseudo-metal layer due to the phenomenon of disorder (non-thermal melting). The laser pulses excite the electrons of the valence band (VB) towards the conduction band (CB) which induces an electronic imbalance in the materials, and to reach its equilibrium the ions will move to find a new vibrational position. This random motion of the ions is called non-thermal fusion (the disorder). After a certain number of laser pulses the dielectric materials takes a metallic character because of a high electronic density in the conduction band which influences the optical properties of the surface such as the reflectivity $R$ as shown in Fig. 1 with

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2},$$

where $n = \frac{1}{\sqrt{2}} \left[ \varepsilon_{pm1} + (\varepsilon_{pm1} + \varepsilon_{pm2})^{\frac{1}{2}} \right]^2$ is the real part of the refractive index and $k = \frac{\varepsilon_{pm2}}{2n}$ is the absorption coefficient.

The figure 1 represents the reflectivity of the pseudo-metal layer during the irradiation as a function of the electron-hole plasma density at different wavelengths.

The figure 1 represents the reflectivity of the pseudo-metal layer during the irradiation. We observe an increase in reflectivity as a function of electron-hole plasma excitation which indicates that the Sapphire surface takes a metallic character with high free electrons density. Note that this increase in reflectivity does not represent the effect of the nanostructure on absorption but it is due to plasma electrons induced during irradiation.

We also observe that the reflectivity increases with the wavelength decreasing, and then the electrons excitation rate is to be higher at low wavelengths.

The figure 2 represents the evolution of the periodicity of nanostructure HSFL type via the generalized plasmonic model described above. Since this model is implicit, we track the evolution of the periodicity according to the increase of the electrons density during the irradiation knowing that the excited electrons density increases when the the pulses number increases.
Figure 2. Calculation of LIPSS period evolution as a function of electron-hole plasma excitation by varying the dielectric surrounding medium (m), at wavelength 300 nm (a), 400 nm (b), 600 nm (c), 800 nm (d), 1000 nm (e) and 1200 nm (f). X is the fraction corresponding to $\varepsilon_{pm} = -\varepsilon_{air}$ or $\varepsilon_{sa}$ where Y is the period, then (X, Y) represent FON or LON.

During the irradiation by multipulses (fs) laser, a very intense electric near-field is induced at the surface of Sapphire due to the non-uniform distribution of electrons density (because the
laser is Gaussian in space) which implies a random nanoablation at the surface [12]. When the condition \( \varepsilon_{pm} = -\varepsilon_{air}(m = 0) \) is reached, the First Ordered Nanostructure (FON) can be observed, e.g. \( \Lambda_{FON} = 87.07 \text{ nm at } \lambda = 300 \text{ nm} \) (Fig. 2(a)). This corresponds to the minimum Plasmon Resonance \( RP_{\text{min}} \). This \( RP_{\text{min}} \) is caused when the plasmons tend to coherently couple with the incident laser wave at the pseudo-metal/air interface.

The electrons density continues to increase when the pulses number increases to until it reaches the condition \( \varepsilon_{pm} = -\varepsilon_{sa}(m = 1) \) where we can observed the smallest nanostructure or the Last Ordered Nanostructure (LON), e.g. \( \Lambda_{LON} = 38.23 \text{ nm at } \lambda = 300 \text{ nm} \) (Fig. 2(a)) which correspond to the maximum Plasmon Resonance \( RP_{\text{max}} \).

Figure 3 represent a recapitulation of all periods can be observed in Sapphire surface during multipulse femtosecond laser irradiation with varying wavelengths between 300 nm and 1400 nm.

Figure 3. The First Ordered Nanostructure FON (black line) and Last Ordered Nanostructure LON (red line) as a function of \( \lambda_L \), where the area marks the possible period \( \Lambda \) between them.

We observed in Fig. 3 that the range of nanostructures periods increases when the wavelength increases, which implies that the possibility of observing nanostructures is greater at larger wavelengths. As the period of the nanostructures increases with the wavelength, this improves the trapping of the incident waves, and therefore the surface absorption of micro-solar cell can be enhanced with high periods nanostructures [19].

Figure 4 represent the penetration depth of the irradiated wave, and it is also represents the depth of the pseudo-metal layer as a function of the electron-hole plasma excitation at different wavelengths, where \( \delta = \frac{c^2}{2\omega k} \).

Girolami et al [19] proposed that the absorption of the micro-solar cells can be enhanced if the pseudo-metal layer depth increase. However, Fig. 4 shows that the depth of the pseudo-metal layer is tens of nanometers and it can be enhanced with larger wavelength. The pseudo metal layer remains a mix state (from the point of view of the dielectric function) between air and bulk Sapphire when \( (m < 1) \), therefore at \( (m = 1) \) (\( RP_{\text{max}} \)) the irradiated depth transformed totally
Figure 4. Penetration depth of the irradiated wave as a function of electron-hole plasma excitation at different wavelengths.

to metal-like phase [11, 20], So at this point, all the absorbed energy at the pseudo-metal layer with depth $\delta_{\text{max}}$ to be reserved to the SPP excitation which can enhance the surface absorption.

4. Conclusions

In this paper, we have demonstrated the efficiency of our generalized plasmonic model when it is used in following the evolution of periodic nanostructures of HSFL type in dielectric material such as Sapphire, at wavelengths between 300 nm and 1400 nm, and its accuracy and efficacy on a nanoscale has been proven. The results show that the period of the nanostructures and the depth of the pseudo-metal layer increase with the increase of the femtosecond laser wavelength. Therefore, we can conclude that the surface absorption of Sapphire can be enhanced with large wavelength, which is suitable for the applications in micro-solar cells devices.

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