The evidence of the role of surface plasmon polaritons in formation of femtosecond highly-regular laser-induced periodic structures on Cr films

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Abstract. Cr films of controlled thickness deposited on glass substrates were irradiated by a high number of low-intensity femtosecond laser pulses below the Cr single-pulse damage threshold, producing periodic surface structures (LIPSS) of very high regularity via metal oxidation. To address the multiplicity of electromagnetic modes allowed for thin films, a rigorous numerical approach for modeling surface plasmon polaritons (SPP) in thin-film geometry has been developed. Three types of modes are predicted: the classical SPP with periodicities $\Lambda \sim \lambda$ ($\lambda$ is laser wavelength) at air-film interface, and $\Lambda \sim \lambda/n$ at film-substrate interface ($n$ is refractive index of substrate), and a propagation mode $\Lambda \sim \lambda/n_C$, where $n_C$ is refractive index of film material. Experimentally observed LIPSS periods match well the predicted modes for the extreme cases, $A \sim \lambda/n$ at film thickness $h \leq 30$ nm and $A \sim \lambda$ at $h \geq 200$ nm, indicating respectively the dominance of SPP excited at the film-substrate interface and at the metal surface. For $30$ nm < $h$ < 200 nm, decreasing of the film thickness results in transition from the pure surface mode to its coupling with and finally domination of the electromagnetic wave excited at the film-substrate interface, providing evidence of the SPP mechanism of LIPSS formation under laser irradiation of thin metallic films.

1. Introduction

By scanning surfaces with high-repetition rate femtosecond laser pulses, highly regular periodic surface structures (LIPSS) can be formed at rates, which are competitive with existing industrial standards [1-4] in nanostructure demanding applications. The physical origin of the highly regular LIPSS was recently linked with the lossy properties of irradiated materials, where SPP decay length for propagation along the surface is small enough, thus limiting the interference of the multiple SPP excited at randomly distributed scattering centers in different parts of the laser-irradiation spot [4]. Whereas a number of lossy metallic materials enable the formation of highly regular LIPSS [1-4], low-loss plasmonic metals exhibit a lower quality LIPSS [4-6].

In this work, LIPSS were produced on Cr films of controlled thickness deposited on glass substrates by a high number of low-intensity femtosecond laser pulses below the Cr single-pulse
damage threshold via metal oxidation (referred below as thermochemical LIPSS or TLIPSS). A systematic study of the role of film thickness on the TLIPSS period has been performed. The experimental results are analyzed based on an advanced thin-film SPP (TF-SPP) model, which accounts for the interference between SPPs excited at two film interfaces: with air and glass substrate. Simulations reveal that, depending on the film thickness, two possible electromagnetic modes can be responsible for TLIPSS formation: (1) SPP generated at the film-substrate interface for very thin films and (2) SPP excited on the film free surface for relatively thick films. The transition between these two modes suggested by the TF-SPP model and observed experimentally provides the evidence of the important role of SPP excitation upon laser irradiation of thin metallic films.

2. Experimental results

The experiments on TLIPSS formation were carried out on the setup described in detail in [7]. Femtosecond laser pulses with a central wavelength of 1026 nm, duration of 232 fs, and repetition rate of 200 kHz were focused by a lens with $f = 35$ mm providing the beam diameter $\approx 15 \mu m$ on the surface. The pulse energy $E_p$ was in the range 100-110 nJ. The sample translation speed was set to 1 µm/s. Metal films were deposited on BK7 borosilicate glass substrates by the magnetron sputtering technique which provides controlled film thickness $h$ in the range of 28-350 nm. Scanning electron microscopy (SEM) Hitachi TM3000 was used to inspect nanostructures formed on the sample surface.

**Fig. 1.** The results of TLIPSS formation on chromium film with thickness of 28 nm at different scanning speeds: 1 µm/s (b), 50 µm/s (c), 100 µm/s (d), 200 µm/s (e), 300 µm/s (f).

The LIPSS produced on 28-nm Cr film at different scanning velocities $v_s$ are presented in Fig. 1. Regular TLIPSS along the laser polarization direction with the period of 678 nm are formed at low $v_s$ of 1 µm/s - 10 µm/s (Fig. 1a,b). They can be classified as low spatial frequency LIPSS (LSFL) [4]. Increasing $v_s$ to 50 µm/s yields in reducing TLIPSS regularity (Fig. 1c). Under these conditions, the TLIPSS period slightly increases and the non-regular LIPSS on the top of TLIPSS with the direction perpendicular to polarization and the period of ~200-250 nm (high spatial frequency LIPSS or HSFL) becomes pronounced. Increasing $v_s$ to 100-200 µm/s results in merging the adjacent ablative HSFL (Fig. 1d, e). Upon merging, the HSFL regularity increases as clearly seen for $v_s = 300$ µm/s (Fig. 1f).

Comparison of TLIPSS produced on Cr films of different thicknesses is presented in Fig. 2. When increasing $h$ to 70 nm (Figs. 1a and 2a), TLIPSS period increases to 842 nm (Fig. 2b) and to 909 nm on film with thickness of 125 nm (Fig. 2c), while the HSFL are more ordered as compared to thinner films and their average period for this $h$ is 100 nm (Fig. 2d). The comparable period values of HSFL were observed in [8] at laser wavelength of 800 nm and 200 nm thick Ti film, but the orientation of structures in our case is different and perpendicular to the laser polarization direction.

3. Theoretical analysis

SPP properties in thin films can be studied in a simplified manner by solving an implicit equation based on the dielectric permittivities $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$, associated with the propagation wave-vectors $k_i$,
Fig. 2 The results of TLIPSS formation on chromium film with different thickness: 28 nm (a), 70 nm (b), 125 nm (c). The enlarged image of TLIPSS on chromium film with thickness of 125 nm (d).

$k_2$, and $k_3$, respectively [9]. The latter are defined by the light momentum conservation expressed as

$$k_j^2 = \beta_j^2 - e_j \left( \frac{\omega}{c} \right)^2$$

(1)

where $j = 1, 2$ or 3 related to the film material (Cr in our case), air, and substrate respectively; $c$ is light velocity in vacuum/air; $\omega$ is the laser frequency. The periods of possible modes of the surface electromagnetic waves resulting from the interference of the laser wave with the SPP wave is provided by the relation $\Lambda = 2\pi / \text{Re}(\beta)$ where $\beta$ is the complex wave number associated with the SPP modes. The periods can be calculated by numerically solving Eq. (1) with the following equation [10]

$$e^{-2k_{1t}} = \left( \frac{k_1 + k_2}{\varepsilon_1 + \varepsilon_2} \right) \left( \frac{k_1 - k_2}{\varepsilon_1 - \varepsilon_2} \right) \left( \frac{k_1 - k_3}{\varepsilon_1 - \varepsilon_3} \right)$$

(2)

Among the possible wave-numbers $\beta$, we consider the solutions which are associated with a distance characterizing SPP propagation (decay) length $L_{\text{SPP}}$ expressed by $L_{\text{SPP}} = \frac{1}{2\pi \text{Im}(\beta)}$ [10], which is comparable with the spot diameter ($1 \mu m < d < 100 \mu m$). Other modes of nanoscale periods are neglected as they are damped on distances much smaller than laser wavelength.

Figure 3 presents the comparison between the measured LIPSS periods and theoretical predictions. The classical SPP mode with the period $\Lambda \sim \lambda$ is characterized for chromium by $L_{\text{SPP}}$ of the order of several micrometers [4]. For $\lambda = 1026$ nm, assuming a constant dielectric permittivity [11], the properties of SPP at the air/Cr interface are: $L_{\text{SPP}} = 4.06 \mu m$ and $\Lambda = 1026$ nm. For the Cr/BK7 interface, using the optical data from [12], one has $\Lambda = 711$ nm and $L_{\text{SPP}} = 1.34 \mu m$. These $\Lambda$ values are marked by dashed horizontal lines in Fig. 3. The SPP modes at the air/Cr and BK7/Cr interfaces computed by the TF-SPP model are shown by solid lines, red and blue respectively, which are very close to the classical modes. Some increase in periodicity with decreasing the film thickness indicates preferable generation of asymmetric SPPs, according to [13].

Comparison of modeling with the experiment suggests that the laser light couples predominantly with the air/Cr asymmetric SPP mode when film thickness is larger than ~200 nm and with the Cr/BK7 mode when thickness is ≤ 30 nm. Note SPP decay depth $1/|k_1|$ is found ~32.8 nm, slightly larger than the penetration depth of the light in Cr at $\lambda = 1026$ nm (~23 nm). However, in the case when oxidation is active, SPP decay depth should increase. Then the SPP at the air/Cr surface can excite an SPP on the Cr/glass interface and the electromagnetic interaction between the two SPPs cannot be neglected [14]. If it is so, at $30 \text{ nm} < h < 200$ nm, a coupled mode arising from this interaction can drive the TLIPSS formation. With increasing film thickness, the interaction becomes weaker and the transition from Cr/glass to air/Cr mode gradually occurs that is not yet explained by the theoretical results. Returning to Fig. 1, we admit that the HSFL might be attributed to the guided mode in the film whose periodicity follows the tendency $\Lambda \sim \lambda/n_{\text{Cr}}$. The periodicity can change due to partial oxidation that can be treated, e.g., in the frames of effective optical media. However, that still calls for further studies.

**Conclusion**

The thermochemical LIPSS were produced on Cr thin films of different thickness by applying femtosecond-laser scanning at pulse energy below the single-pulse damage threshold. A theoretical
Fig. 3. Comparison between experimental results and theory for $\lambda = 1026$ nm. Measured LIPSS periods (see Fig. 2) are shown by black squares (LSFL) and red circles (HSFL). SPP modes computed by using TF-SPP model are shown by solid lines. Red line is for the SPP mode at the air/Cr interface and blue line is for the SPP mode at the Cr/BK7 interface. Horizontal black dashed lines correspond to $\lambda$ and to the mode associated with light propagation toward the bulk $\lambda/n$ with $n$ to be refractive index of Cr. Vertical lines show the optical penetration depth in Cr (left) and the decay depth of SPP excited at the air/Cr interface (right).

analysis has been performed, which predicts the periods of the possible SPP modes of the films. For film thicknesses larger than 200 nm, the observed LSFL period matches with the air/Cr SPP mode while for thicknesses smaller than 50 nm it matches with the Cr/BK7 SPP mode. Although transition between the two cases is not yet directly described by modeling, these results provide evidence of the SPP mechanism of LIPSS formation under laser irradiation of thin films of lossy metals.

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