Micro-structuring of gold coated plates with LIPSS for localized plasmonic sensors

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Localized surface plasmon resonance (LSPR) or particle plasmon resonance (PPR) consists in a specific arrangement of metallic nanostructures in order to enhance their plasmonic response. This technique can lead to the development of high sensitivity bio-sensors but faces various difficulties on the fabrication side.

We investigate Laser Induced Periodic Surface Structuring (LIPSS) in order to produce sub micron periodic patterns on gold layer for localized plasmonic sensors fabrication. LIPSS are periodic structures that are generally created on a material surface by accumulation of ultra-short pulses exhibiting energies close to the material ablation threshold. Although LIPSS physical mechanisms are still under investigation, they have been induced in a wide variety of materials (metals, semiconductors, polymers, etc) for numerous applications such as realization of hydrophobic/hydrophilic surfaces, control of surface reflection or realization of low friction / high adhesion surfaces. Here we used ultrashort pulses (500 fs) at 515 nm to induce LIPSS structures on thin gold layers for LSPR sensors.

Keywords: LIPSS, Plasmonic, Gold, LSPR

1. Introduction

Localized Surface Plasmon Resonance (LSPR) is a powerful technique for sensitive bio-sensing. LSPR in metals strongly depends on the size and shape of the sensor and can be enhanced with a nanoscale pattern. LSPR sensors can be applied in many applications like chemical, biological sensing… In our case we are targeting the development of a label-free biosensor for plant diseases evaluation at points-of-care [1]. In this work, our team has developed an original microfabrication method involving gold gratings synthesis by pulsed laser writing.
Different other methods have been explored in literature for generating micro and nano periodic structures on gold [2, 3,11] like UV lithography, interferometry, nanosphere lithography, nanoimprint [4,5]. Another solution we are investigating is the use of Laser Induced Periodic Surface Structuring (LIPSS) in order to produce sub-micron periodic patterns on gold for localized plasmonic sensors fabrication.

LIPSS are periodic structures that are generally created on a material surface by accumulation of ultra-short pulses exhibiting energies close to the material ablation threshold. High resolution structures proportional to the laser operating wavelength, typically ripples of hundreds of nanometers, can be generated [6].

2. Description of the experiment

2.1 Laser and micro-machining setup

The micromachining set-up used for the experiments is described in Figure 1. As we can see, the system is made of a laser system followed by three optical modules.

The femtosecond laser used in this experiment operates at a wavelength of 1030nm and delivers optical pulses of energy up to 40µJ at a repetition rate in the range of 10 kHz to 300 KHz. The optical beam generated by this laser will be modified through three different modules before reaching the sample.

The first module permits to change the wavelength of the laser. A second harmonic generation set-up, based on a LBO crystal, is employed in order convert the optical wavelength down to 515nm. This wavelength is more suitable than infrared because of the absorption spectra of Gold and it will permit achieving smaller LIPSS structures.

The second module permits to control the power/energy of the laser beam and its profile. We use a halfwave plate (HWP) and a polarization beamsplitter cube for power control and a diffractive optical element (DOE) for beam shaping. The DOE converts the input beam into a square top-hat beam shape (4x4mm) with a homogeneous energy distribution. A second HWP is placed to control the linear laser polarization orientation.

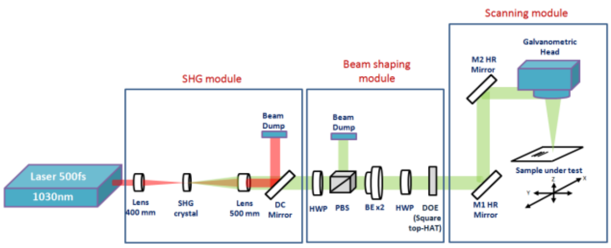

Fig. 1 Laser experiment for LIPSS structuring

The third module consists of the scanning and focusing elements. We used here a 2D scanning galvanometric head equipped with a 160 mm f-theta lens, and coupled with a X-Y-Z translation stages platform to position precisely the sample under laser beam. With this configuration, two techniques are possible for dynamic irradiation of the samples: move the sample using the translation stages, keeping a fixed point of incidence for the focalized laser, or fix the sample position and scan the surface with the galvanometric head. The focused spot size (square shape) is estimated around 25µm.

2.2 Samples description

The samples are made of a thin layer of gold (35 nm) deposited on glass by vapor phase evaporation, with an intermediate 1 nm adhesion layer of Chromium. The Glass is a 1mm thick standard microscope slide. The LIPSS process permitted to generate regular patterns with a periodicity of about 500 nm. Due to the thin layer of gold, careful manipulations and a precise control of the laser energy deposited on the material are needed. Initial surface roughness of a sample is Sa=2nm.

Fig. 2 Samples scheme

2.3 Characterization

The analyses of the irradiated samples were performed with a 3D confocal laser microscope equipped with 20X and 150X objectives, and also with a SEM microscope. The first microscope is useful to have rapid views of the surface and precise estimation of the profile and roughness of the LIPSS generated structures; and the second one is mandatory to see details within the nanometer scale.

3. Main results

3.1 Ablation threshold

The first step of the work was to define the minimum deposited laser energy density on the sample required for removing the thin gold layer, i.e. the ablation threshold.

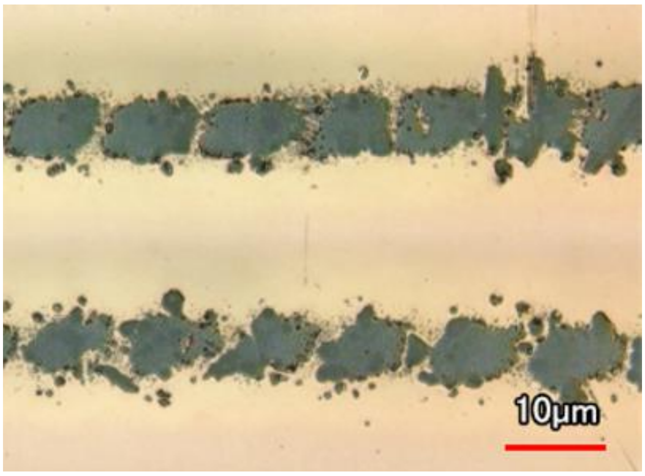

Fig. 3 Ablation of the thin gold layer obtained with a fluence of 0.09 J / cm²

Therefore, we studied the ablation behavior of the material as a function of the laser fluence for a high scanning speed fixed at 1000 mm/s, and for a pulse frequency of 100kHz. This condition makes it possible to separate the laser impacts on the surface and to evaluate an ablation threshold for a single pulse. We then defined the threshold fluence as the minimum value for which an ablation profile is measurable. The ablation threshold was estimated to 0.072 J/cm², which corresponds to an average power of 50mW, which is in-line with literature [6,7]. The main difficulties to evaluate this ablation threshold were that we often have a "peeling off effect" of the gold layer even at very low laser fluence. Experiences conducted us to use the thin Chromium layer as a mandatory adhesive layer.

3.2 Fluence effect

Dynamic studies were performed by adjusting the laser polarization with the HWP so that the ripples produced by LIPSS are oriented perpendicularly to the machining scan lines, and by fixing the laser frequency at 100kHz for three different fluences for a single pulse energy of 0.072 J/cm², 0.058 J/cm² and 0.042 J/cm². This corresponds to average powers of 50, 40 and 30 mW respectively.

This time, we used a scanning speed in the range 10-100 mm/s, giving us an overlap for each laser pulse corresponding to 99-95%

To evaluate the impact of the three fluences on the generated LIPSS structures, we measured the surface roughness Sa on the center of the scanned line (yellow mark on Fig.7)

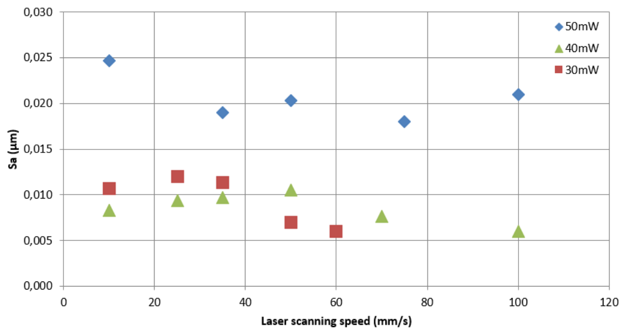

Fig.4 Analysis of LIPPS surface roughness as a function of the scanning speed, for 3 different laser powers @100kHz

Depending on the scanning speed, the overlap is more or less important and the number of pulses varies between 1000 and 10000 pulses/mm. In all presented cases the LIPPS patterns are very regular. The best parameter found is 25mm/s with 30mW average power (0,042J/cm² - 100 pulses). Even if a 10X factor of deposited energy is tested (related to the speed process) and the average value of the surface roughness slightly decreases with the speed, we can see that the highest speed of 100mm/s give us a good pattern structure and also a faster process to generated LIPSS on cm² surface area.

3.3 Laser Frequency effect

We also tried different laser frequencies with different scanning speeds in order to improve the quality and the depth of the LIPSS structure. We compared for the same fluence of a single laser shot of 0.042J/cm² (we adapted the average power of the laser) the repetition rates of 100, 200 and 300kHz.

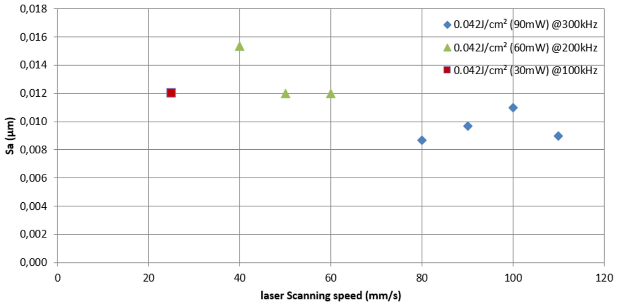

Fig.5 Analysis of LIPPS surface roughness as a function of scanning speed, for 3 different laser repetition rates

The trend observed in the previous paragraph is also valid if the frequency is doubled or tripled (Fig.4) with a slight decrease of the surface roughness, i.e the depth of the LIPSS pattern, with the increase of the speed.

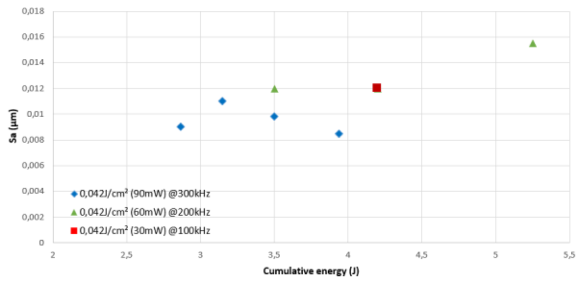

Fig.6 Analysis of LIPPS surface roughness as a function of cumulative energies

This study highlights two different behaviors of the gold thin film under femtosecond irradiation. Within the limits of the parameters studied, the most important parameter is the single pulse fluence since it is this one which determines the evolution that matter will undergo. In a second step, it is the number of overlapped pulses or cumulative energy that allows these micro-structures to evolve (Fig 6).

4. Discussion

We present the analysis of the two best results obtained within this work. We present a case of low spatial period LIPSS (ripples on the surface) but also one LIPSS parameter allowing a periodic ablation of the thin gold layer.

4.1 Best Low Frequency LIPSS obtained

We identified different parameters giving the best ripples for the generated LIPSS, i.e the most periodic, regular and contrasting ones. We measured a periodicity in the order of 520nm, same range than the laser wavelength. These experiments were done with the same single pulse laser fluence around 0.042J/cm², and only the scanning speed and laser frequency change (Fig 5.)

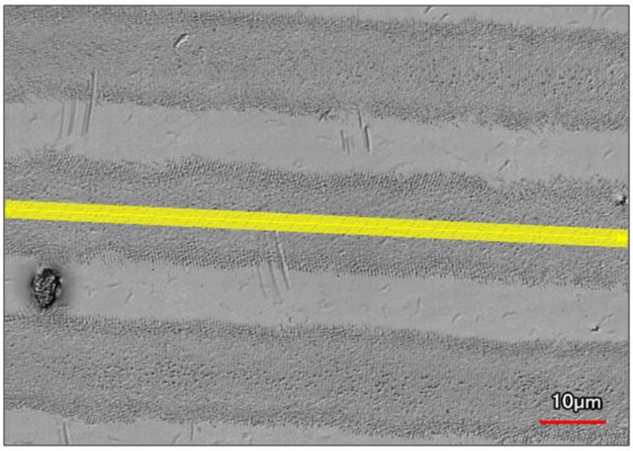

Fig.7 Analysis for LIPSS with 0,042J/cm² with a laser scanning speed of 80mm/s, 300kHz

The light intensity distribution on the focused laser spot, although having certain homogeneity thanks to the DOE, is not so clean particularly at low fluence. You can see sometimes different ripples and patterns from LIPSS at the borders of the scanning lines (Fig 7.)

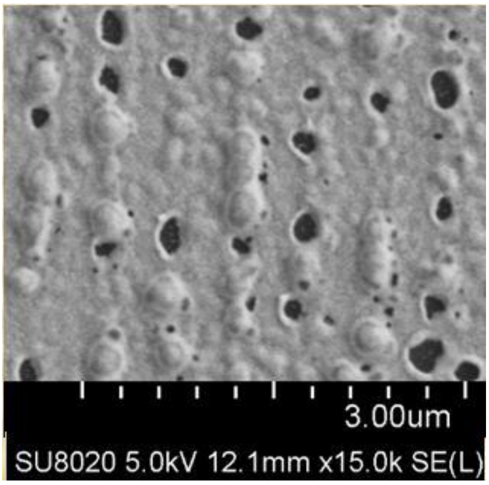

Fig.8 SEM analysis for LIPSS with 0,042J/cm², 80mm/s 300kHz

The SEM analysis reveals that the periodic structures of the LIPSS are made of an arranged structure of bubbles and holes.

4.2 Periodic ablation

Here we present the laser and scanning parameter for which we observed a complete ablation of the layers of gold and chromium. Compared with the previous experiments, we worked this time above the ablation threshold, and with high speed, trying to limit the effects of total ablation on LIPSS generated structure.

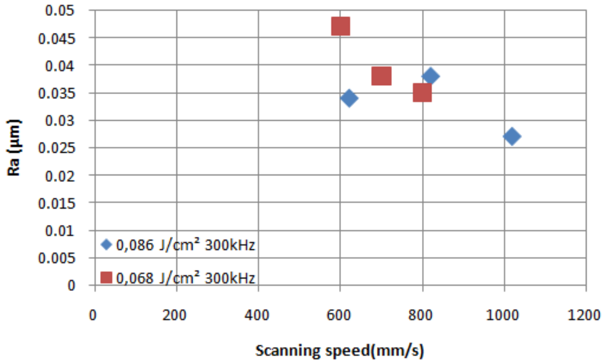

Fig. 9 Linear Roughness Ra vs scanning speed for 6 different parameters showing periodic ablation

We observe that the gold streaks, perpendicular to the laser scanning direction, are homogeneous. By analyzing their profiles (Fig 9), we observed that their depth is very close to the thickness of the gold and chromium layers, i.e. a depth of about 35nm.

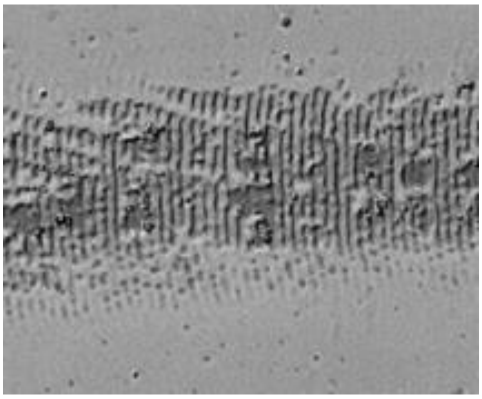

Fig. 10 Periodic ablation for LIPSS with 0,086J/cm², 300kHz, 820mm/s.

We measured also a periodicity in the order of 520nm. Nevertheless, a SEM analysis of the sample reveals that the lines are not very homogeneous, which affects the periodicity analysis.

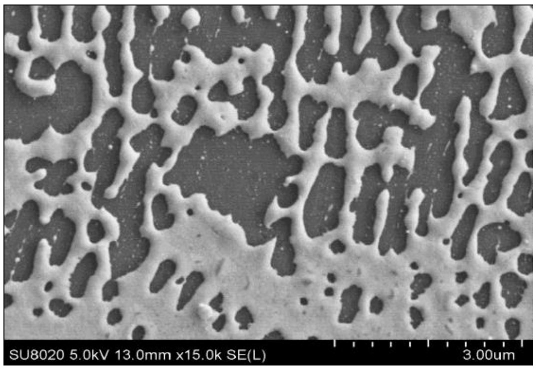

Fig. 11 SEM analysis for Periodic ablation for LIPSS with 0,086J/cm².

5. Conclusion

We have studied the different steps of the self-organization of matter resulting from dynamic irradiation by a femtosecond laser with Yb doped fiber doubled along a line on the surface of a thin layer of gold of 35nm. The formation of LIPSS oriented perpendicular to the radiation lines was carried out.

The analysis of these samples with a scanning electron microscope reveals that the reliefs of the wavelets are peaks and aligned holes. The explanation advanced by the literature to explain the weak clarity of LIPSS on gold is the too weak coupling electron-phonon which results in the diffusion of the electrons before they transferred their energy to the matrix. [6,7]

The main obstacles encountered during this work were the extreme sensitivities of the parameters. Indeed, a small variation of the thickness of the gold layer, or of the laser pulses energy, leads to a large variation in the morphology of the observed structures. We would next try to carry out specific periodic structures with points spaced from each other by the same distance. For these realizations, circular polarization or the creation of cross patterns with perpendicular wavelet directions, are promising lines of research.

Another technique will be Laser-induced reorganization [11] using our LIPSS process, but in this case our samples need to be adapted to this technique.

Acknowledgments

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