Machine translation

2. (WO2018010707) METHOD AND SYSTEM OF ULTRAFAST LASER WRITING OF HIGHLY-REGULAR PERIODIC STRUCTURES

PCT Biblio. Data | **Full Text** | National Phase | Notices | Drawings | Documents

Description

Title of Invention : Method and system of ultrafast laser writing of highly-regular periodic structures

Technical Field

[0001] The present invention relates generally to periodic surface structuring via laser ablation and more particularly to generating highly-regular periodicity of nanostructures on metallic surfaces at high processing rates by means of providing a high degree of coherence of the surface electromagnetic waves.

Background Art

[0002] Nanostructures are structures of intermediate size between microscopic and molecular objects, usually referred to a few up to hundreds of nanometers at least in one spatial dimension. In general, a nanotechnology is a technical field dealing with manipulation of matter on an atomic, molecular and supermolecular scale. By term manipulation, it is particularly meant technological goal of precisely manipulating atoms and molecules for fabrication of macroscale products.

[0003] With increasing demand for nanostructured materials, the technology of fast preparation and processing has been raising. But, the currently pending problem is to find an appropriate method for fast and cheap preparation of highly regular periodic structures (HR-PS) on material surfaces.

[0004] The known methods involve irradiation of solid targets by ultrashort laser pulses which leads to the formation of Laser-Induced Periodic Surface Structures referred usually as LIPSS. These structures represent a periodic surface relief whose orientation is directly connected with polarization of the laser light. LIPSS can be formed on the surfaces of different materials (metals, semiconductors, dielectrics, polymers).

[0005] LIPSS-based applications have already emerged during the last decade such as color marking, change in surface wettability, and growth of biological cells. However, two main problems still exist, which prevent further implementation of these structures in various fields such as microelectronics, optoelectronics, photovoltaics. There is increasing demand for structural uniformity and high rate of their imprinting into material surfaces.

[0006] Currently known LIPSS technology suffers from loss of regularity, appearance of double periodicity, and numerous bifurcation points. Quantitatively, the surface structural periodicity can be mathematically described by applying the 2-Dimentional Fast Fourier Transform (2D-FFT) analysis of Scanning Electron Microscopy (SEM) or Atomic Force Microscopy (AFM) images. An average period (or wavelength) of the structures is determined as the inverse of the peak position of the 2D-FFT and regularity of the period is characterized by the dispersion angle of FFT signal. The most regular structures achieved by the present time on only one material, Cr (*A. Ruiz de la Cruz, R. Lahoz , J. Siegel, G.F. de la Fuente, J. Solis, High speed inscription of uniform, large-area laser-induced periodic surface structures in Cr films using a high repetition rate fs laser, Opt. Lett. 39, 2491-2494 (2014)*) are still imperfect. The method used in the mentioned document does not preserve high regular period from one to another line of structure on large area (dispersion angle of 2D-FFT is ~26.5°±1.8°).

[0007] The laser-induced periodic surface structures are a subject of following documents:

[0008] The patent document US7875414 discloses a method of periodic structure formation on extensive area with a uniaxial laser beam. The method uses a laser fluence above but nearly as low as ablation threshold. Moreover, the overlapped scanning is set such that the number of pulses of the laser beam irradiated on an identical position of the material surface is within a range of 10 to 300, but it is not still enough to achieve the high regularity and fast producing.

[0009] The patent application US20080216926 refers to structures on metallic materials but the method does not provide regularity of periodic structure.

[0010] It should be mentioned that none of them are directly referring to high-speed writing of highly-regular periodic structures on large area.

Summary of Invention

[0011] The present invention provides a method for obtaining periodic structure on a surface of a substrate, said method allowing ultrafast writing by the laser, and achieves highly regular periodic structures having preferably an angle dispersion of FFT signal smaller than 15º. The periodic structure with the periodicity between λ and λ/2, wherein λ is the laser wavelength, is provided by the method of the invention, which does not show any bifurcation point. The periodic structure having an angle dispersion of FFT signal smaller than 15º and not showing any bifurcation points are referred herein as a highly regular periodic structure.

[0012] The invention provides a method for obtaining a periodic structure, preferably with the dispersion angle of FFT signal less than 15˚, on a surface of a substrate, using a pulsed laser beam having a wavelength λ, wherein

[0013] the substrate is provided; the substrate is being made of material having an imaginary part of dielectric permittivity equal or higher than the absolute value the real part of dielectric permittivity for the laser beam wavelength λ; and

[0014] a spot on the surface of the substrate is irradiated using the pulsed laser beam, wherein:

[0015]

- the laser pulse duration of said laser beam is less than the time required by electrons in the substrate for thermalization with a lattice; and
- the pulsed laser beam is linearly polarized to induce surface electromagnetic waves propagating on said surface along the polarization direction; and
- the diameter of the irradiated spot on the substrate´s surface is smaller than or equal to three characteristic decay lengths of said surface electromagnetic wave; and
- fluence of the pulsed laser beam is higher than the ablation threshold.

[0016] The fluence is selected so that strong the ablation of the substrate is induced with avoiding formation of excessive volume of molten substrate, whereby ablation occurs with preserving the said periodic absorption profile on the metallic surface, thus forming highly regular periodic structure.

[0017] The wavelength λ of the laser beam is typically in the spectral range from UV (e.g., from 100 nm) to mid-IR (e.g., from 10 µm).

[0018] The term substrate designates a material onto which the periodic structure is applied. The substrate is also commonly called „material", „target", „sample" in the field of the art.

[0019] The method as described herein is based on determining and achieving conditions necessary for creating the highly regular periodic structure. The conditions as follows:

[0020] As a first condition, for efficiently driving the free electrons by the pulsed laser beam, the laser pulse duration must be less than the time that electrons take in the substrate until their thermalization with lattice. Typically, the laser beam pulse duration will be at subpicosecond duration range but it may be also extended to several picoseconds.

[0021] As a second condition, the size of the illuminated area must be smaller than or equal to three characteristic lengths of the surface electromagnetic waves (SEW) decay, which is typically ≤30 µm, depending on the substrate material. In this case, the free electrons driven into motion by the SEW oscillate coherently over the whole illuminated area, thus securing highly periodic absorption of laser energy within the illuminated area with periodicity along light polarization.

[0022] The characteristic SEW decay length L must be of order of the laser spot size used to generate the structures. Accounting for exponential decay of SEW, the laser spot size on the substrate surface has not to exceed $3L$. The SEW decay length is given by the expression

[0023] $L = 1/(2\times\mathrm{Im}(\beta))$, (1)

[0024] where $\beta = 2\pi(\varepsilon/(\varepsilon+1))^{0.5}/\lambda$ at the air-substrate interface. The dielectric permittivity ε is given by experimental measurements and also available in literature as known by a person skilled in the art.

[0025] By comparing the SEW decay length L of the substrate with the regularity of the obtained highly-regular periodic structures (measured by a quantity $\delta\theta$ describing the dispersion over orientation angle of the parallel structures in respect of the used laser polarization), an excellent correlation was found.

[0026] As a third condition, the laser fluence higher than the ablation threshold applied to the small illuminated area provides large amplitude of the absorption pattern culminated by the regime of strong ablation, driven by enhanced mechanical stresses in radial direction, already at single laser pulses that allows to avoid formation of excessive volume of molten material remaining on the surface after ablation. Strong ablation followed by quick solidification of remaining shallow melt preserves the regular periodic absorption profile on the metallic surface, thus forming highly regular periodic structure. The single-pulse laser fluence has to be sufficient to melt material and induce its developed ablation and can be from fraction of J/cm^2 to several J/cm^2 (e.g., up to 20 J/cm^2) depending on the ablation threshold of particular material at particular wavelength.

[0027] As a fourth condition, the dielectric permittivity ε of the substrate must exhibit a high damping, i.e. the imaginary part of dielectric permittivity is close to or higher than the absolute value of its real part for the considered irradiation wavelength λ, as expressed by the following equation:

[0028] $\mathrm{Im}\,[\varepsilon(\lambda)] \geq |\mathrm{Re}\,[\varepsilon(\lambda)]|$ (2).

[0029] Typically, metallic substrates obey this condition.

[0030] Once the single illumination event results in highly regular periodic structure formation, the next laser pulse can overlap with the previous one only partially, by few structure periods, reproducing the periodic structure on the new illuminated area via inducing coherent electron oscillations which are pre-defined by overlapping with the structured area. It is preferred that the overlap is at least 30 % of the spot area, more preferably at least 50 % of the spot area.

[0031] For this, the scanning speed and the repetition rate of the laser should be adjusted so that the overlap of two spots irradiated one after another is provided. High scanning speed and high repetition rate (e.g., higher than 1 kHz, preferably about 1 MHz) are particularly suitable for industrial use of the invention. High scanning speed can be achieved for example by employing galvanometric scanning head or another high speed scanner, e.g., based on the fringe projection technology, preferably in combination with a translational stage.

[0032] The relatively small overlapping between illuminated areas and scanlines sufficient to produce highly regular periodic structures enables high scanning speed of substrate structuring provided for example by the scanning technique which combines a high-speed scanner and translation stage. Polarization of the laser light can be at any angle relative to scanning direction.

[0033] The present invention provides a fast and cheap production method for writing of the HR-PS on large areas of substrate surfaces. Surface periodic structures are formed as a result of interference of incident and scattered surface electromagnetic waves (SEW) followed by self-organization effects which do not lead directly to regular periodic structures. Further technical problem solved by this invention is to minimize of negative influence of the processes involved in the periodic structure formation (thermoplastic deformations, non-thermal melting) and ablation mechanisms (spallation, phase explosion, Coulomb explosion). The Method of Direct Formation of Highly-Regular Structures on Metallic Materials provides activation of Surface Electromagnetic Wave (SEW) interfering with the incident laser wave at the surface of the substrate in a manner which ensures high quality and regularity of the obtained pattern.

[0034] The above mentioned problem disappear with the method carried out with the present invention, more particularly when diameter of the irradiated spot is smaller or equal to 30 micrometres and/or the laser pulse duration of the laser beam is smaller or equal to 10 picoseconds, more preferably it is lower than 1 picosecond.

[0035] In one embodiment, for the laser beam wavelength of less than 1300 nm. The following materials are suitable as the substrate: Cr, Fe, Mo, Ni, steels, Ti, W, alloys thereof.

[0036] In one embodiment, for the laser beam wavelength of less than 900 nm. The following materials are suitable as the substrate: Be, Bi, Co, Cr, Fe, Mo, Nb, Ni, steels, Ti, V, W, alloys thereof.

[0037] In one embodiment, for the laser beam wavelength of less than 500 nm. The following materials are suitable as the substrate: Ag, Au, Be, Bi, Co, Cr, Cu, Fe, Mo, Nb, Ni, Pt, steels, Ta, Ti, V, W, alloys thereof.

[0038] The present invention thus further provides a product made by above described method.

[0039] According to another aspect of the present invention, a device adapted specifically for carrying out the method of the invention is provided.

[0040] Said device for producing a periodic structure on the surface of a substrate comprises:

[0041] means for generation of a pulsed laser beam with pulse duration smaller than 10 ps and high repetition rate;

[0042] an f-theta lens, wherein the f-theta lens is capable of focusing the laser beam to irradiate an area with a diameter of up to three characteristic lengths of the SEW decay;

[0043] a galvanometric scanning head, said galvanometric scanning head enables a high coherence of surface electromagnetic waves; optionally comprising a translation stage (e.g., motorized) for placing the substrate;

[0044] a polarizer; and

[0045] a half-wave plate rotatable with respect to the polarizer.

[0046] The rotation of the polarizer and of the half-wave plate controls the direction of the laser-induced structure.

[0047] The translation stage (xy-stage or xyz-stage) provides for translational and/or rotational movement of the substrate.

[0048] In one embodiment, the device may further comprise an attenuator positioned so that the laser beam generated from the means for generation of the pulsed laser beam is directed to the attenuator, a telescope, and means for directing the laser beam from the attenuator to the telescope. The telescope allows, located in front of the scanning head of galvanoscanner, to increase the aperture of the beam with the use of positive focal length lenses or that are separated by the sum of their focal lengths and, thus, to achieve focusing of the laser beam to an exact and sufficiently small illuminated area.

Brief Description of Drawings

[0049] Fig.1 illustrates an example of a device for ultrafast laser writing of highly-regular periodic structures on substrate surface.

[0050] Fig. 2 illustrates the scheme of laser beam expanding based on the telescope principle.

[0051] Fig. 3 illustrates the scheme of laser beam focusing.

[0052] Fig. 4 illustrates the direction of the produced structures relative to the polarization and scanning directions whose mutual orientation can be arbitrary.

[0053] Fig. 5 illustrates overlapping of illuminated spots in a scanline and between scanlines upon scanning the substrate surface.

[0054] Fig. 6 illustrates the typical view of highly-regular periodic structures on metallic substrate, molybdenum as an example.

[0055] Fig. 7 illustrates an example of the algorithm of the method.

[0056] Fig. 8 summarizes the requirements for selection of materials able to exhibit Highly-Regular Periodic Structures upon pulsed laser irradiation at 1030 nm wavelength: (a) shows the SEW decay length of materials; (b) presents the dielectric permittivity of materials which satisfy the selection criteria).

Description of Embodiments

[0057] The invention is herein further illustrated by way of examples which should not be construed as further limiting.

[0058] In one example, as shown in the figure 1, there is a device comprising an ultrafast laser system **1** with pulse duration of order or smaller than 10 ps and high repetition rate. The energy per pulse is selected in order to overcome the ablation threshold of the material under treatment with the mean of attenuator **3**. The beam **2** is directed to the telescope comprising a pair of lenses **6** and **7**, with a sequence of mirrors **4** and **5**. After the telescope, the expanded beam **2** is deflected on the surface of substrate **12** by means of a galvanometric scanning head **9** connected to a f-theta lens **10**. The rotation of a half-wave plate **8** with respect to a polarizer **11** allows defining the direction of the laser-induced structures. The laser beam **2** was focused on the substrate surface **12** and scanned by galvanoscanner head **9** to an extent related to the focal length ***F*** in order that deflection of the beam **2** is negligible. Much larger areas were obtained by moving the sample with a motorized xyz-stage **13** under galvanoscanner **9**.

[0059] The proposed setup allows obtaining both regular and irregular structures with aspect ratio depending on the material **12**. The use of linearly polarized light makes possible to obtain quasi-regular linear structures with periodicity below the wavelength of the laser beam.

[0060] The factors that permit to obtain highly-regular structures are: Laser spot diameter, not more than three characteristic lengths of the SEW decay length. This enables to maintain the coherence of laser-excited electrons within the ablated structures for subsequent laser pulses.

[0061] The methods to decrease the laser spot are: increasing aperture of the beam **2** before the galvanoscanning head **9** by means of a telescope, as shown in Fig. 2, comprising two lenses **6** and **7** that expand the beam **2** coming from direction **14**.

[0062] In another example, as shown in Fig. 3, the focusing f-theta lens **10** decreasing the laser spot is presented.

[0063] Angle between polarization direction ***E*** and scanning direction ***S*** is schematically shown in Fig. 4. Polarization direction ***E*** is oriented perpendicularly to the desired direction of the structures to be obtained.

[0064] Maintaining overlap between the illuminated spots and between scanning lines was solved in preferred embodiment as shown in Fig. 5. The different scanlines must overlap in order to maintain coherence between the structures on the earlier processed surface and the new one.

[0065] The optimal laser fluence was estimated depending on the substrate **12** in order to obtain the material ablation and to avoid excessive volume of melt substrate **12**. Small illumination spots are favouring a deeper ablation of substrate **12** due to higher radial stresses compared to larger spots.

[0066] Fig. 6 illustrates a SEM image of HR-PS. The shown sample was produced by method of scanning the surface of molybdenum with the wavelength of 1030 nm, pulse duration of 213 fs, laser energy of 0.75 J/pulse, 62% overlap between pulses and 50% overlap between scanlines.

[0067] Fig. 7 illustrates the requirements for ultrafast laser writing of highly-regular periodic structures on metallic substrate **12**. Column I summarizes usual conditions for periodic structure formation on metallic surfaces. Extremely high writing speed on large area (Column II) together with small illumination spots overlapping along scanline and overlapping between scanlines (Column III) allow to achieve high regularity of periodic structures.

[0068] Fig. 8 illustrates an example of selection of materials for HR-PS writing at wavelength of 1030 nm based on the analysis of the mechanism of their formation. The structures originate from the excitation of Surface Electromagnetic Waves (SEW) at the surface of metallic materials. Materials allowing for such possibility share specific criteria disclosed in summary of invention. In the Figure the materials are presented whose SEW decay length is smaller than 10 μm and which possess high optical damping. It is thus disclosed that the spatial coherence of the excited SEW within the laser illuminated spot is at the origin of the high regularity of the obtained periodic structures. The SEW can be initiated by any sub-wavelength scattering center. The scattering centers can be a point-like defect, a dipole-like nanotip forming the sample roughness, a bigger object like a nanoparticle present at the surface, or even a scratch. By using a small spot size, excited SEWs interact on a small area where spatial coherence can be conserved. The distance of the excited SEW is linked with the decay length *L* of the SEWs. The usage of a small spot size allows triggering selectively the excitation of short-range SEWs.

Industrial Applicability

[0069] Ultrafast laser microprocessing of surfaces of different materials is a growing technology for a variety of industrial applications, such as photovoltaics, photonics, micro- and optoelectronics. The periodic surface nanostructuring opens new niches for laser surface processing in industrial applications. The method may be used for solar cells structuring, writing surface waveguides, optical gratings, light extracting surfaces in light emitting diodes, surface enhanced Raman scattering, water-repellent surfaces, marking for products anti-counterfeiting. All listed applications require the fabrication of large-area, highly-regular and uniform periodic structures at high writing speed that is proposed in the present disclosure which solves the problems of low writing speed and low quality of periodic structures.

Claims

[Claim 1] A method of obtaining a periodic structure, preferably with the dispersion angle of FFT signal less than 15°, on a surface of a substrate (12), using a pulsed laser beam (2) having a wavelength λ, **characterized in that**, the method comprises the steps of:
- providing the substrate (12) being made of material having an imaginary part of dielectric permittivity equal or higher than the absolute value of its real part for the laser beam wavelength λ; and
- irradiating a spot on the surface of the substrate (12) by the pulsed laser beam (2), wherein
- the laser pulse duration of said laser beam (2) is less than the time required by electrons in the substrate (12) for thermalization with a lattice; and
- the pulsed laser beam (2) is linearly polarized to induce surface electromagnetic waves propagating on said surface along the polarization direction; and
- the diameter of the irradiated spot on the substrates (12) surface is smaller than three characteristic decay lengths of said surface electromagnetic wave; and
- fluence of the pulsed laser beam (2) is higher than the ablation threshold.

[Claim 2] The method according to claim 1, wherein the irradiation of the surface of the substrate (12) is performed by irradiation of a plurality spots, wherein the spots partially overlap each other, preferably said plurality of spots are arranged in at least one line and the laser beam (2) scans over the at least one line.

[Claim 3] The method according to claim 1 or 2 further comprising the step of increasing an aperture of the pulsed laser beam (2) and subsequent focusing of the laser beam (2) to the surface of the substrate (12).

[Claim 4] The method according to any one of the preceding claims, wherein a diameter of the irradiated spot is smaller or equal to 30 micrometres.

[Claim 5] The method according to any one of the preceding claims, wherein the laser pulse duration of the laser beam (2) is smaller or equal to 10 picoseconds, more preferably it is lower than 1 picosecond.

[Claim 6] The method according to any one of the preceding claims, wherein the laser beam wavelength is less than 1300 nm, and the material of the substrate (2) is selected from the group consisting of: Cr, Fe, Mo, Ni, steels, Ti, W, alloys thereof.

[Claim 7] The method according to any one of claims 1 to 5, wherein the laser beam wavelength is less than 900 nm, and the material of the substrate (2) is selected from the group consisting of: Be, Bi, Co, Cr, Fe, Mo, Nb, Ni, steels, Ti, V, W, alloys thereof.

[Claim 8] The method according to any one of claims 1 to 5, wherein the laser beam wavelength is less than 500 nm, and the material of the substrate (2) is selected from the group consisting of: Ag, Au, Be, Bi, Co, Cr, Cu, Fe, Mo, Nb, Ni, Pt, steels, Ta, Ti, V, W, alloys thereof.

[Claim 9] A product by process according to anyone from the preceding claim.

[Claim 10] A device for producing a periodic structure on a surface of a substrate (12) comprises:
- means for generation of a pulsed laser beam (2) with pulse duration smaller or equal to 10 ps and repetition rate higher than 1 kHz;
- means for scanning and delivering the pulsed laser beam (2) to the substrate (12), preferably a galvanometric scanning head (9);
- a polarizer (11);
- a half-wave plate (8) rotatable with respect to the polarizer (11); and
- means for focusing the pulsed laser beam to the substrate (12), preferably f-theta lens (10).

[Claim 11] The device according to claim 10, wherein the means for generation of a pulsed laser beam (2) have a repetition rate at least 1 MHz.

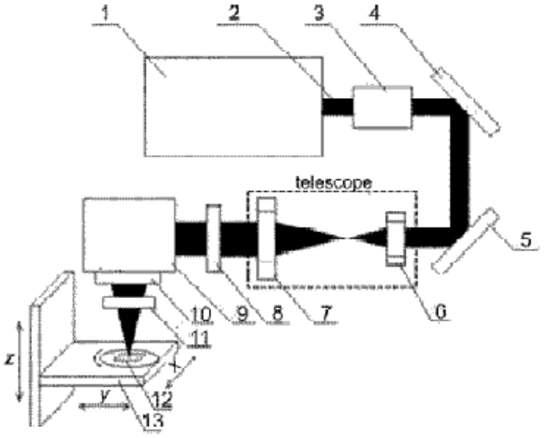
[Claim 12] The device according to claims 10 to 11 further comprises a telescope located between the means for generation the pulsed laser beam (2) and the means for scanning and delivering the pulsed laser beam (2) to the substrate (12).

[Claim 13] The device according to any one of claim 12 further comprises an attenuator (3) located between the means for generation the pulsed laser beam (2) and the means for scanning and delivering the pulsed laser beam (2) to the substrate (12) and/or between the means for generation the pulsed laser beam (2) and the telescope.

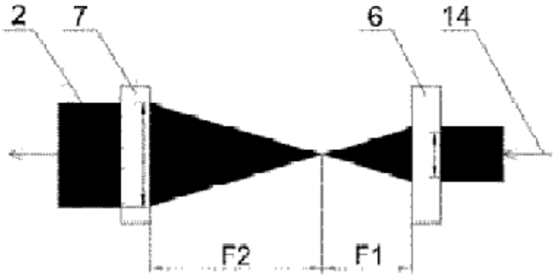
[Claim 14] The device according to claims 12 or 13, wherein the telescope comprises a pair of lenses (6) and (7).

[Claim 15] The device according to anyone from the claims 10 to 14 further comprises a motorized xyz-stage (13) capable of translational and rotational movement of the substrate (12).

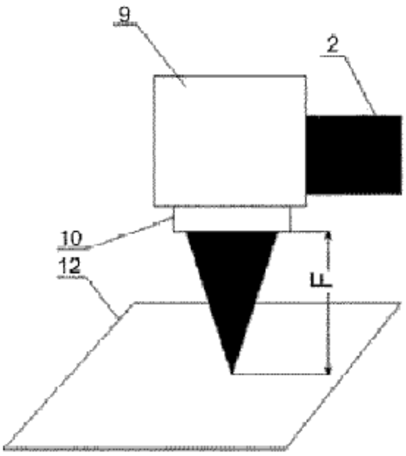
Drawings



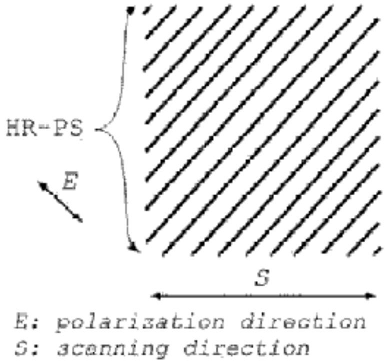
[Fig. 1]



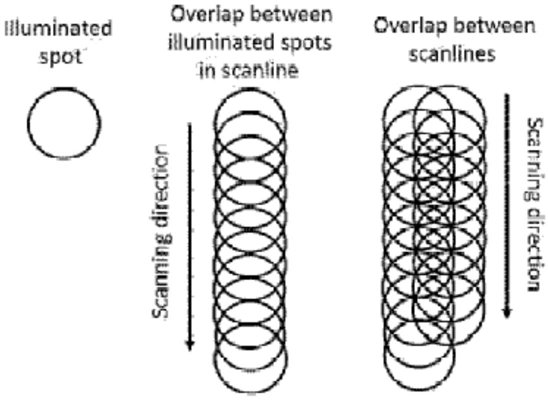
[Fig. 2]



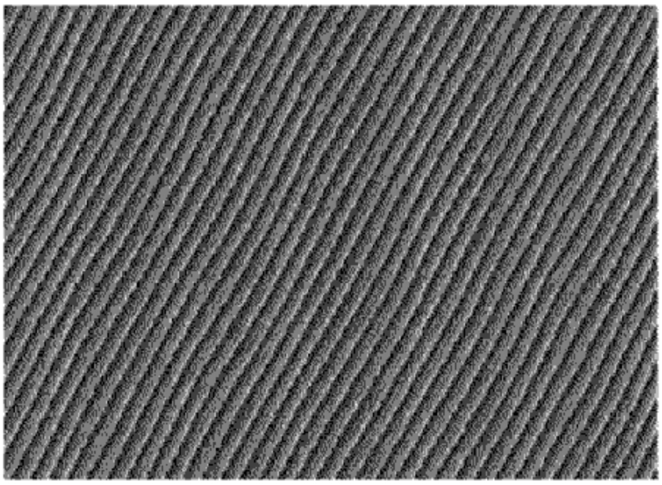
[Fig. 3]



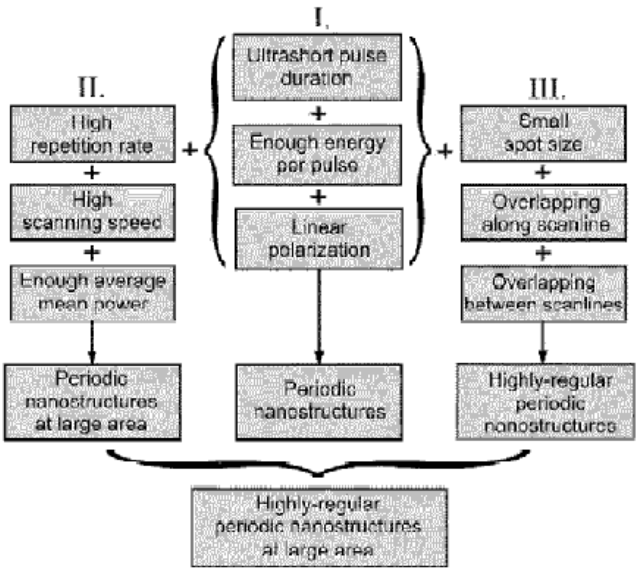
[Fig. 4]



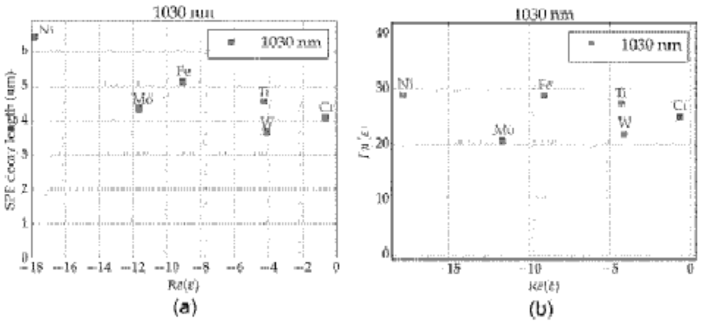
[Fig. 5]



[Fig. 6]


I.
Ultrashort pulse duration
+
Enough energy per pulse
+
Linear polarization
II.
High repetition rate
+
High scanning speed
+
Enough average mean power
III.
Small spot size
+
Overlapping along scanline
+
Overlapping between scanlines
+
+
Periodic nanostructures at large area
Periodic nanostructures
Highly-regular periodic nanostructures
Highly-regular periodic nanostructures at large area

[Fig. 7]


1030 nm
1030 nm
SPE decay length (um)
Ni
Mo
Fe
Ti
W
Cr
0
1
2
3
4
5
6
−18
−16
−14
−12
−10
−8
−6
−4
−2
0
Re(ε)
1030 nm
1030 nm
Ni
Mo
Fe
Ti
W
Cr
0
10
20
30
40
15
10
5
0
Re(ε)

(a)

(b)

[Fig. 8]