

# Prospects for The Use of Nanotechnology for The Manufacture of Optical Meta-Materials.

O.D. Volpyan<sup>1</sup>, A.I. Kuzmichev<sup>2</sup>, Yu.A. Obod<sup>3</sup>, A.S. Sigov<sup>3</sup>

<sup>1</sup>LLC Fotron-Avto Scientific Production Complex, Russia, Moscow

<sup>2</sup>National Technical University of Ukraine "Kiev Polytechnic Institute", Ukraine, Kiev

<sup>3</sup>MIREA - Russian University of Technology, Moscow, Russia

## Abstract

Nanotechnology methods for obtaining 2D and 3D meta-materials are considered. The main attention is paid to the methods of forming submicron and nanometer structures using nanotechnology methods, first of all laser methods. It is shown that these technological methods, being planar and scalable, are promising for use in industrial optical production due to their potentially high productivity and low cost compared to many other methods of nanotechnology, in particular, with electronic lithography and processing with focused ion beams.

**Keyword:** nanotechnology, materials, high productivity, processing.

## 1.Introduction

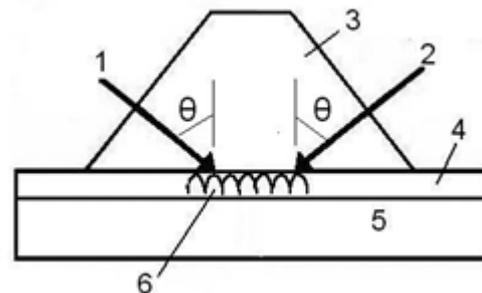
For the manufacture of meta-materials promising and, as a rule, single nanotechnology, first of all, it should be paid attention to the laser technology. In the optical wavelength range, the sizes of meta-atoms have submicron / nanometer values. This required the use of nanotechnology methods for the manufacture of optical meta-materials, and only with the development of these methods in the last decade has it become possible to obtain samples of optical meta-materials. This article is a review of nanotechnology, primarily laser, which can be used to manufacture optical meta-materials.

## 2.Research methods

For the manufacture of optical meta-materials, it is possible to implement interference laser photo-thermal lithography, which allows the creation of gratings of nanometer elements (holes or protrusions on the surface of the substrate) from a dielectric, metal or semiconductor [1, 2]. This method of lithography is based on the thermal effect of light (melting and evaporation) at the points of the interference pattern with the maximum intensity of radiation. As an example, consider an experiment [2] with a sample — a silicon wafer coated with its oxide with a thickness of 80 nm; a layer of polycarbonate (~ 50 nm) and a film of indium with a thickness of 10 nm are deposited on it. A XeCl laser ( $\lambda = 308$  nm) with an average specific radiation power of 20 mW / cm<sup>2</sup> was used. The interference of four coherent rays on the surface of an 'In film' resulted in the formation of a two-dimensional array of holes in the film during a pulse duration of 10. The minimum size of the hole was about a quarter  $\lambda$ . Then the polymer layer was etched in oxygen plasma through the holes in the 'In film', which served as a protective mask during this operation. After that, it was possible to pickle holes in the silicon oxide layer using

plasma chemistry with the transfer of the hole sizes in India. In [2], it was shown that using an analogous method, an array of nanometer holes (with a diameter less than 100 nm) can be created in a GaAs substrate covered with a SiO<sub>2</sub> layer (the average pulse energy density of a XeCl laser with  $\lambda = 308$  nm on the substrate surface was about 3 J / cm<sup>2</sup> with a pulse duration of 20 ns). Obviously, with such pulse duration, the requirements for the mechanical stability of the installation and laser sources are sharply reduced.

Lithograph by evanescent waves is based on the use of non-propagating damped near-field waves, which are called evanescent waves in the English-language literature. Near-field lithography allows one to overcome the diffraction limit and obtain an image of subwave-sized elements. In recent years, interest has been shown in the application of interference of resonant evanescent waves of the near field of diffraction gratings or prisms for recording holograms [3] and for the purposes of lithography [4-6]. The disadvantages of this method include reduced image contrast and a small depth of exposure. Figure (1) shows the scheme for the implementation of interference in photoresist-evanescent waves generated due to the effect of disturbed total reflection of two laser beams falling on the base of a prism from a high-refractory material ( $n = 1.745$ ) at an angle  $\Theta$  that is greater than the angle of total internal reflection.



**Figure 1.** Diagram of the device with interference of evanescent near-field waves of a prism with full internal reflection based on [4]. 1, 2 — laser

beams, 3 — triangular prism (60°), 4 — photoresist layer (240 nm), 5 — silicon substrate, 6 — interference of evanescent waves.

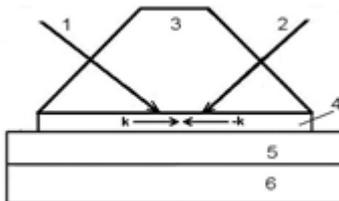
The parameters of 1D strip gratings obtained by irradiation with two rays, and 2D point gratings obtained by irradiation with four rays, are shown in Table 1.

**Table 1.** Comparison of characteristics of various types of interference lithographs [6]

View lithography	Dual beam interference			Three-beam interference		
	Period NM	Resolution NM	Thickness NM	Period NM	Resolution NM	Thickness NM
IL	253	136	300	246	128	300
EV	187	97	100	164	82	100
SPT (AG)	175	93	180	164	82	160
SPT (AL)	175	93	200	164	82	180

IL - laser interference lithography (Fig. 3), EV - lithography by interference of evanescent waves (Fig. 4), SPT - lithography of surface Plasmon (Fig. 5). Ar laser was used. Exposure time: IL - 0.4 s; EV - 0.3 s; PP - 3 s (Ag) and 25 s (Al)

Plasmon lithography (interference of surface Plasmon) uses surface Plasmon. As is known, surface Plasmon are oscillations of the charge density of free conduction electrons on a metal surface; their full name is surface plasmon polaritons (SPP) [7]. They are excited at the interface between the dielectric prism and the metal due to the effect of impaired total internal reflection. The metal is a thin film of a well-conducting metal deposited on the base of a prism (Figure 2). Under resonant conditions (at a certain angle of incidence of the laser beam), a strong electric field arises at the metal-photoresist interface due to the connection between the SPT and the evanescent wave. Strengthening the field leads to an increase in the thickness of the irradiated photoresist layer and an increase in contrast compared with lithography with evanescent waves. In Figure 2, the arrows ( $k$  and  $-k$ ) show the wave vectors of the RFP, excited by both laser beams.



**Figure 2.** Diagram of the device with the interference of surface plasmon ( $k$  and  $-k$ ) [31]. 1, 2 — laser beams, 3 — triangular prism (60°), 4 — metal film (50 nm, Ag or Al), 5 — photoresist layer (240 nm), 6 — silicon substrate.

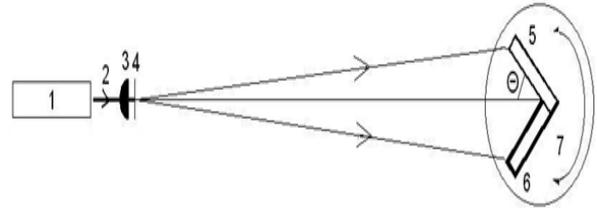
For the experiments, the same triangular prism was used, as in the experiments with evanescent waves. To obtain a good optical contact between the metal film and the photoresist, an immersion liquid with an intermediate refractive index was worn on the latter. The parameters of 1D strip gratings obtained by irradiation with two rays, and 2D point gratings obtained by irradiation with four rays, are shown in Table 1.

Table 1 also shows the characteristics of conventional laser interference lithography (IL) obtained under the same conditions. The data presented show that near-field interference lithography (with evanescent fields and RFP) provides a better resolution than conventional laser interference lithography. However, plasmon lithography irradiates a greater thickness of the photoresist and creates a stronger contrast compared with lithography with evanescent waves; this allows the use of RFP for the manufacture of thicker structures. Also note that in near-field lithography, the effect of reflection from the substrate surface does not manifest itself (as is the case with conventional laser lithography) due to the attenuation of the field on the way to the substrate. Finally, we note that in all cases, only an 'Ar' laser flash was enough to carry

out the lithographic process. As a result, these types of lithographs make it possible to produce submicron and nanometer structures that do not require masks (templates), high-performance, and low-sensitivity to mechanical stress (vibration) and less expensive when used in industrial production.

Lloyd interferometer-based interference systems are also effective for laser lithography.

A diagram of a laser lithographic setup based on the Lloyd interferometer is shown in Figure 6.

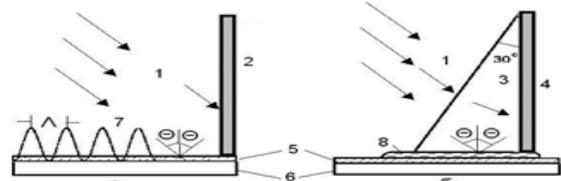


**Fig. 6.** Diagram of a lithographic setup based on the Lloyd interferometer [9]. 1 — laser, 2 — ray of light, 3 — lens, 4 — a diaphragm with a small-diameter hole, 5 — a mirror, 6 — a substrate with a deposited photoresist, 7 — a rotating table.

A continuous laser 1 generates an s-polarized light beam 2 with high longitudinal coherence. The laser radiation passes through the lens 3 and the diaphragm 4, which create a diverging beam, and falls partially on the mirror 5 and partially on the substrate 6. The central axis of the beam is directed to the line of contact between the mirror and the substrate. The angle between the mirror and the substrate is 90°. The mirror and the substrate are mounted on a table 7, which can be rotated. The interference of the direct beam coming from the laser with the beam reflected from the mirror occurs on the surface of the substrate. Turning the table leads to a change in the period of the interference pattern. The period of the painting is determined by the well-known formula. The lithographic installation based on the Lloyd interferometer, due to the presence of a rotating table, provides ample opportunities in the creation of interference patterns and objects [8]. For example, the use of the second exposure with the rotation of the table allows you to create isolated lines, cubic and hexagonal structures of dielectric or metal columns and holes. A rotation of 90° between the exposure procedures with the same period creates a cubic lattice; rotate 60 - hexagonal structure with elliptical columns and holes. To obtain a circular shape, two mirrors are used at an angle of 120°. You can make a crystal-like structure with other types of lattices.

### 3. Analysis of results

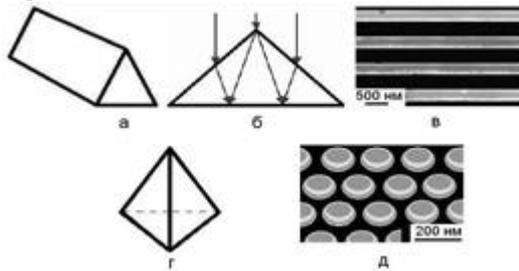
It has been repeatedly noted that the presence of an immersion substance (other than air) on the surface where interference occurs leads to a decrease in the period of the interference pattern. Therefore, it was proposed to implement this approach in the Lloyd interferometer [9]. For this, a Littrow prism was inserted into it, as shown in Figure 3b. For comparison, Figure 3a shows the scheme of a standard Lloyd interferometer.



**Figure 3.** Diagrams of lithographic installations based on the Lloyd's interferometer [9]: a - standard, b - with a Littrow prism. 1 — laser radiation, 2 — mirror, 3 — Littrow prism with a mirror applied, 4, 5 — photoresist layer, 6 — substrate, 7 — interference pattern, 8 — immersion liquid.

The right side of the prism 3 is equipped with a mirror 4, so the reflection from the mirror occurs inside the prism. Between the prism and the photoresist is an immersion liquid - water to match the refractive indices.

Let us give examples of the use of interference lithography for the manufacture of large area meta-materials. We illustrate the use of laser interference lithography in the manufacture of two samples (1D and 2D) of a magnetic meta-material with negative magnetic permeability [10]. Figure 5 shows the prism (a) and the pyramid (d) used to implement two- and three-beam lithographic systems, respectively. A glass prism or pyramid ( $n = 1.6$ ) was placed above the substrate covered with a layer of photoresist.



**Figure 5.** The use of laser interference lithography in the manufacture of 1D (ab) and 2D (d-e) magnetic meta-materials [10]: a is a glass prism, b is a beam path in a prism, c is a sample of 1D meta-material, d is a glass pyramid d - a sample of 2D material.

The beam of a solid-state single-mode laser ( $\lambda = 532$  nm) with a power of 10 W was expanded with a telescope and directed to the upper surface of the prism (or pyramid), as shown in Figure 5b, and at the interface the base of the prism-surface of the photoresist interfered with light rays positive photoresist. Optimal contrast was obtained with linear s-polarization in the case of a prism and two-ray interference, while pyramid and circularly polarized radiation were used for three-beam interference, which was obtained by converting from linear.

The exposure time was 3-4 minutes. In the process of development, the photoresist was removed in places of light, and in these places the surface of the glass substrate was exposed (its area was  $2.2 \times 2.2$  cm<sup>2</sup>). Then, layers of Au (20 nm) - MgO<sub>2</sub> (60 nm) - Au (20 nm) were sequentially deposited by electron-beam evaporation, after which the residual of photoresist with condensate on it was removed with a solvent. On the surface of the substrate, only the structural elements of the meta-material (magnetic resonators), shown in Figure 5 (e), remained in the places of exposure. These resonators provided negative magnetic permeability (0.7 ... 1.3) at a wavelength of about 1.2 microns.

The obtained meta-material was deposited on a large surface of  $\sim 1$  cm<sup>2</sup> (the area of the substrate was  $2.2 \times 2.2$  cm<sup>2</sup>, which is much larger than the area of samples obtained by the method of electron-beam lithography or ion-beam sputtering). There are other examples of the manufacture of meta-materials using interference lithography [11, 12]. The limited scope of the review did not allow combining laser-based methods for manufacturing optical meta-materials [13], in particular, combining laser lithography with self-assembling processes (processes of self-assembling of structures from colloidal nanoparticles, sometimes called colloidal lithography) [13].

13. Boltasseva A., Shalaev V.M. *Metamaterials*, 2.1 (2008).

## 4. Conclusion

Basic laser technologies of meta-materials and related structures are considered. Laser technologies allow obtaining structures with submicron and nanometer size elements. They have a number of obvious advantages over other beam methods for the fabrication of nanostructures, first of all, over electron lithography and processing with a focused ion beam among which are higher performance and lower cost, the ability to obtain structures on substrates of a large area. It is very important that the considered technologies are planar and scalable, which allows them to be integrated into the existing production of optical-electronic devices and materials.

The work was financially supported by the Ministry of Education and Science of the Russian Federation (the research project "Optical transistors based on meta-materials." The grant agreement with the Ministry of Education and Science of the Russian Federation of September 29, 2016 No. 14.577.21.0219, unique identifier PNIER RFMEFI 57716 X 0219) was made.

## References

- [1] Volpyan, OD, Kuzmichev, A. I. "Negative refraction of waves. Introduction to the physics and technology of electromagnetic metamaterials / Ed. GmZverev. - K.-M. : Avers, 2012.-360 p.
- [2] Bredikhin V.I., Burenina V.N., Verevkin Yu.K., Kirsanov A.V., Petryakov V.N., Vostokov N.V., Dryakhlushin V.F., Klimov A.Yu. *JTP*, 74, 86 (2004).
- [3] Tan C., Peng CS, Pakarinen J., Pessa M., Petryakov VN, Verevkin Yu.K., Zhang J., Wang Z., Olaizola SM, Berthou T., Tisserand S. *Nanotechnology*, 20, 125303 (2009).
- [4] Sainov S., Anne E., Carole E., Lounnot D.J. *J. Opt. A. : Pure Appl. Opt.*, 5, 142 (2003)
- [5] Blaikie R.J., McNab S.J. *Appl. Opt.*, 40, 1692 (2001).
- [6] Martinez-Anton J.C. *J. Opt. A. : Pure Appl. Opt.*, 8, S213 (2006).
- [7] Sreekanth V.K., Chua J.K., Murukeshan V.M. *Appl. Opt.*, 49, 6710 (2010).
- [8] Feth N., Enkrich C., Wegener M., Linden S. *Opt. Express*, 15, 501 (2006).
- [9] Xia D., Ku Z., Lee S.C., Brueck S.R.J. *Adv. Mater.*, 23, 147 (2011)
- [10] Chua J.K., Murukeshan V.M., Tan S.K., Lin Q.Y. *Opt. Express*, 15, 3437 (2007).
- [11] Zhang S., Fan W., Malloy K.J., Brueck S.R.J., Panoiu N.C., Osgood R.M. *J. Opt. Soc. Am. B*, 23, 434 (2006).
- [12] Ku Z., Brueck S.R.J. *Opt. Express*, 15, 4515 (2007).