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CONDENSED MATTER

UV LIGHT CONTROLLED SURFACE MODULATION OF POLYMERIC FILMS

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Abstract. Nanostructures creation and investigation by local irradiation of polymeric (photoresist) films with UV laser light is presented. The structuring of polymeric (photoresist) films surface relief under the action of laser radiation is investigated using Atomic Force Microscopy. Modulation depths from 7–10 nm to hundreds of nanometers were observed and correlated to the laser fluence and/or number of incident laser pulses. We obtained surface relief gratings of complex structure as a function of light intensity distribution in the irradiated material. They can be used as template for material deposition or as scaffold for living cells culture.

Keywords: single step light-induced material structuring, UV laser, photoresist, surface relief gratings.

1. INTRODUCTION

Polymeric materials have a wide domain of applications, from microelectronics and optoelectronics to biology and medicine. In this field photoresist materials are well known and widely used in microelectronic industry. Due to the continuous miniaturization in various fields such as microelectronics, optoelectronics, bio-technologies connected with photonic crystals technology, metamaterials and the guidance of biologic material, it was developed the concept of integration. It means that different functions are realized by devices sustained by the same substrate, which can have also a role in the general scheme of functions. Another step in this concept is nano-integration, and the problem becomes to reduce the dimensions of the integrated devices and the new technologies that have to be developed for this purpose. The problem of obtaining such integrated devices has to be studied from two interconnected points of view: the material with the desired characteristics and the creation of the structure able to fulfil the needed functionalities.

From the point of view of materials many researches have demonstrated surface structuring on poly (ethylene terephthalate), poly (butylene terephthalate), polystyrene [1, 2], hybrid sol-gel glasses [3], materials based on carbazole chromophores in order to develop a plastic blue laser emitting around 400 nm [4], polymers containing azo-benzene groups [5]. We have studied surface relief modulation on azopolymers [6–9] and a structure modelling for scatterometric characterization of photo induced surface relief gratings was developed [10, 11]. We considered that surface modulation of the studied azo-polymers is a result of the supramolecular systems reorganization, due to the conformational changes induced by the photo-isomerisation processes under UV light irradiation [8, 9]. If we take into consideration the molecular modelling studies of the polymeric chains, when azobenzene moieties changed their configuration under UV light (from *trans to cis*), it is assumed that there are some conformational modifications of the entire polymeric chains level, that can generate the supramolecular reorganization.

In this work we present our results regarding surface relief structures formation on commercial photoresist. Photoresists are the most common materials used in the microelectronics industry. They are polymeric materials, generally used as thin or thick films, designed to change their properties upon exposure to light. But the continuous need of miniaturization and highly integrated functionality related also with the need to use ecological processing methods resulted in the last decade in new processing methods.

A general accepted technique for micro and nanoscale processing technologies in microelectronics is lithography, which is the exposure of a photoresist to a light pattern followed by a developing stage (a two steps method). A single step laser patterning method is laser ablation, with the advantage of the high processing speed and the possibility of patterning as well small or large areas. But this method is changing locally the material properties, and in some applications it is important to preserve the composition and structure of the host material. A single step processing method for surface modulation as diffraction gratings has been developed for special applications and was reported [4, 12, 13]. The diffraction gratings are important components due to their broad range of applications in integrated optics.

In this work our interest was focused to analyze single step surface relief gratings with submicron up to 1 μm period produced on photo-resist films. The photo resist (type AZ 5214E and SU 8) films deposited on substrate by spin coating have a thickness of about 1.2–2 μm. The gratings were obtained using laser irradiation at 193 nm wavelength and 7 ns pulse length from an ArF laser, and at 355 nm wavelength and 5 ns pulse length laser radiation from a YAG-Nd laser that was applied to photoresist films through a phase mask with 1,090 or 250 nm period. The interference field was formed just after the phase mask where the film was placed.

2. EXPERIMENTS AND RESULTS

The laser fluence used to print the surface structure is below the ablation threshold of the material and, as a result, the surface structure is continuous, without breaks, cracks or phase changes. Generally, polymeric materials have a good absorption in the UV region of the spectrum, so the light induced effects are very efficient. The in situ reflection of a He-Ne laser and Atomic Force Microscopy (AFM) and optical microscopy analyses of the irradiated region evidenced the gratings formation in the irradiated region.

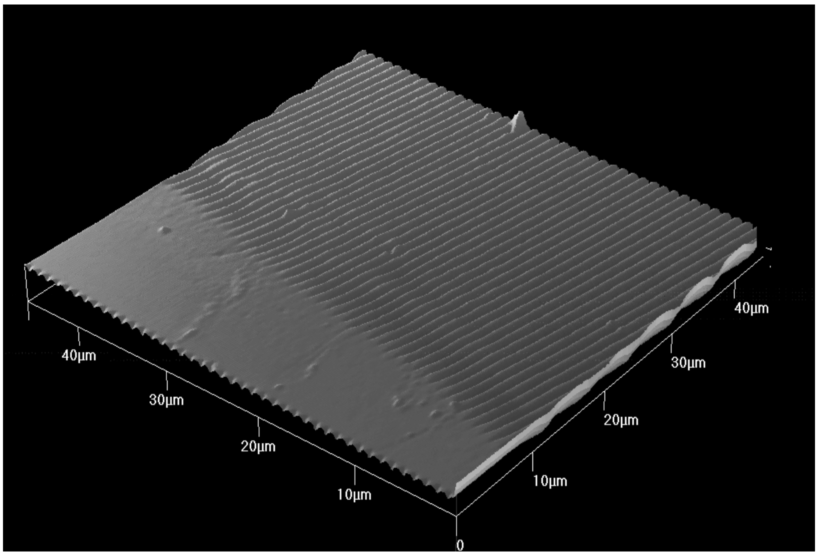
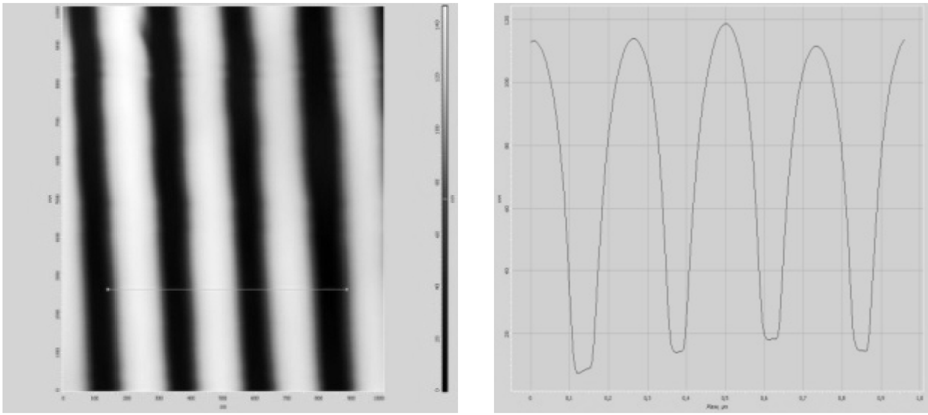


Fig. 1 – AFM image of the border of the single step SRG induced on the surface of the photoresist film under the action of 193 nm laser interference field.

In Fig. 1 is presented an AFM image of a single step laser induced surface relief grating (SRG) at the border where the irradiation ceases. We have obtained a clear surface relief modulation organized as a grating on the material surface, of good uniformity and contrast.

Under the action of 193 nm laser radiation interference field with an incident fluence of approximately 5 mJ/cm^2, using a 250 nm pitch grating mask, we have obtained very good surface relief gratings of 250 nm step. The irradiation time was between 1 min and 4 minutes at 1 Hz. The maximum modulation depth is about 110 nm (Fig. 2). The various magnifications of the AFM images show the good uniformity of the pitch and modulation depth of the grating. The approximately 10% variations in the amplitude of the modulation depth may be the result of the fact that the deposition method of the photoresist film is not assuring a perfectly plane and uniform film. The values for the fluence and the intensity noticed for each irradiation are an average value over the whole surface of the irradiated area.

The evolution of the surface modulation and surface relief grating formation process may be evidenced from the comparative analyses of the AFM images for different irradiation times for the same incident fluence (Fig. 2). It can be seen that for the lower irradiation time the modulation depth is an order of magnitude lower and surface relief structure is less uniform.



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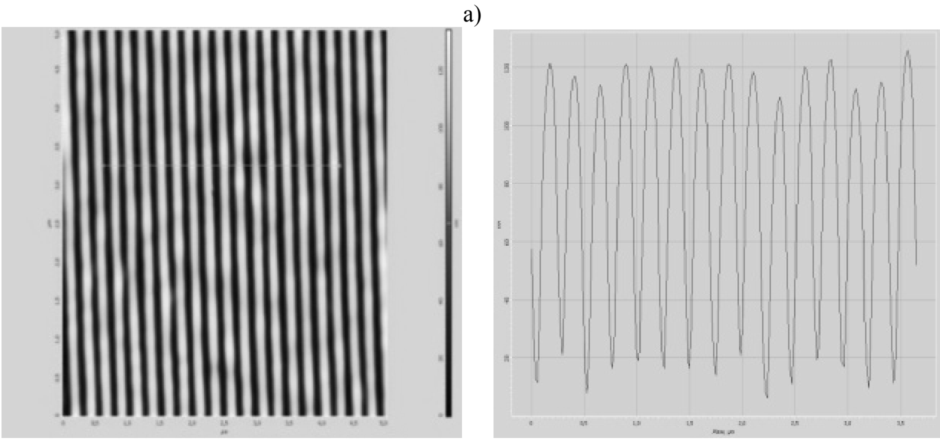

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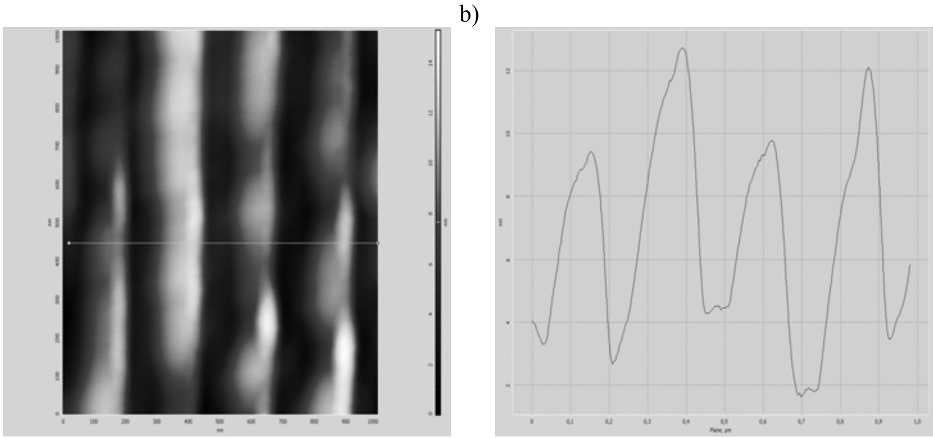
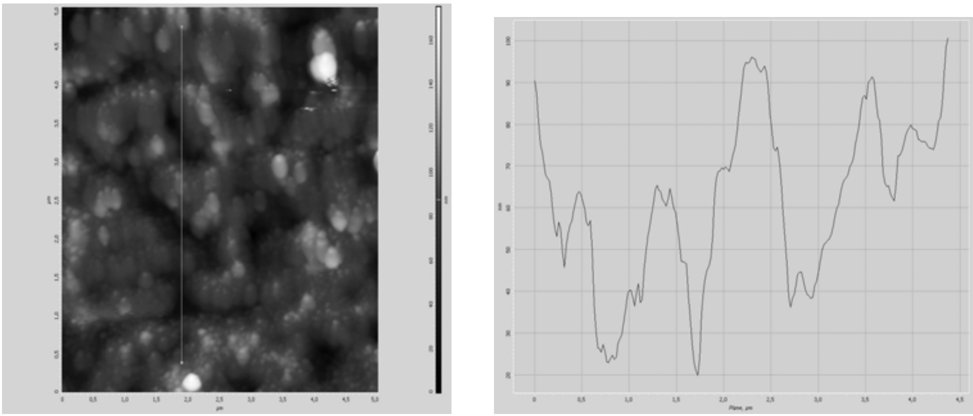


c)

Fig. 2 – AFM image and profile of the 250 nm pitch surface relief grating obtained on the photoresist film (SU8.2). Irradiation conditions: irradiation wavelength – 193 nm, incident fluence – 5 mJ/cm^2, irradiation time / modulation depth: a) 4s /105 nm; b) 4s/90 nm; c) 1s / 7–9 nm.



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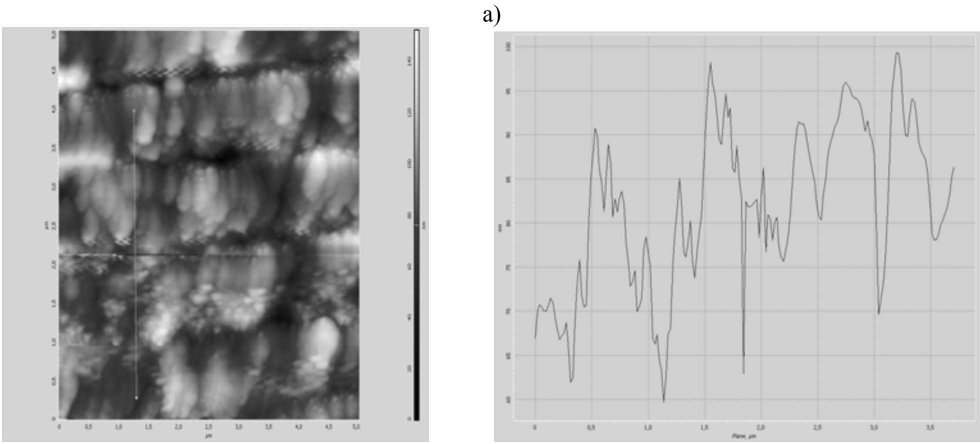

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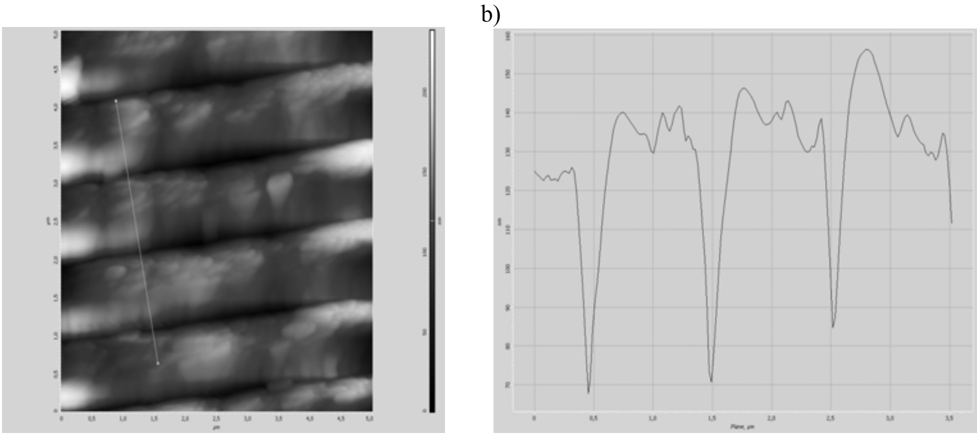

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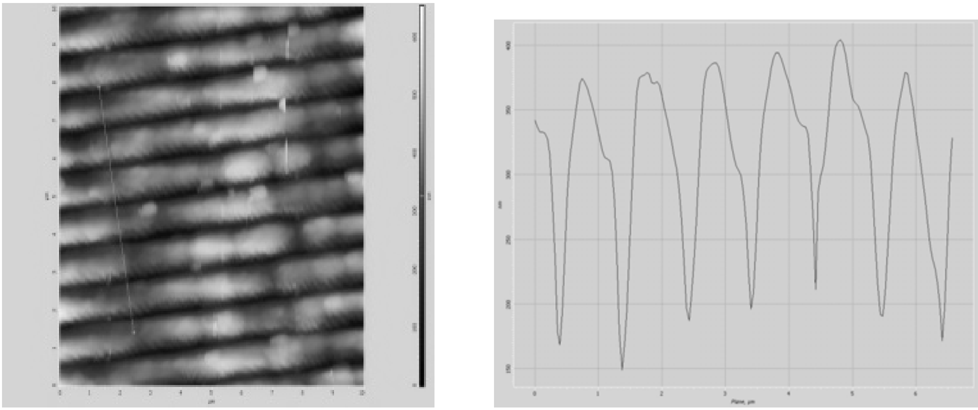
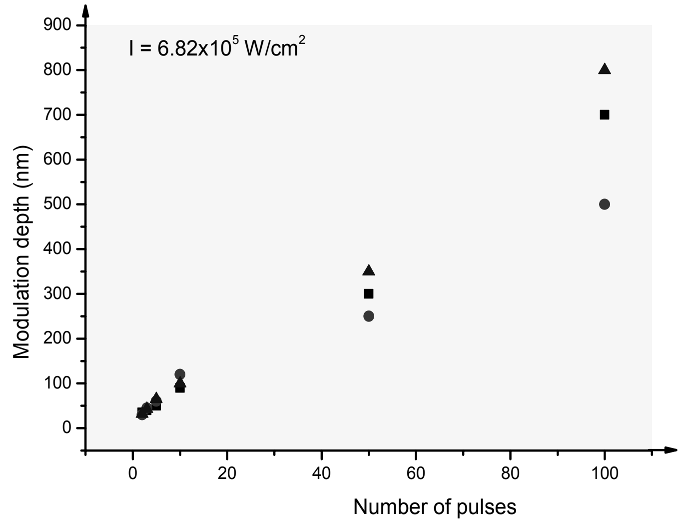


d)

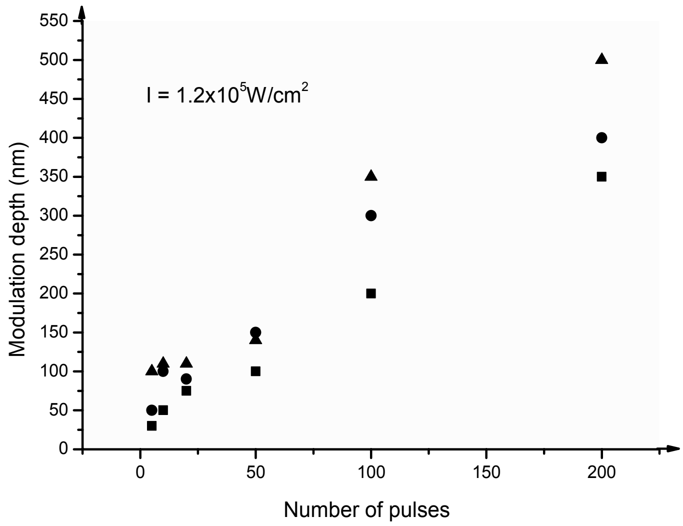
Fig. 3 – Surface relief evolution as a function of irradiation pulses number; material: photoresist AZ 5214E; irradiation wavelength 193 nm. Induced structure: grating with 1 μm pitch; irradiation conditions: fluence 5 mJ/cm^{2}; pulse number/modulation depth: a) 2 pulses / 30–35 nm; b) 4 pulses / 40–70 nm; c) 8 pulses / 60–80 nm; d) 20 pulses/180–200 nm.

To optimise the single step surface relief gratings production a study of the surface relief spatial uniformity and modulation amplitude dependence on the irradiation conditions was realised.

To have an image of the evolution in surface modulation organization from disorder to order we have selected AFM images and AFM profiles of irradiated regions with a constant incident fluence and a growing number of pulses on photoresist AZ 5214E (Fig. 3). For 2 irradiation pulses on the photoresist surface appear “disordered hills” of 30–35 nm height. During 20 pulses the modulation is ordered and a regular structure appears. The dependence of the modulation depth of the 1 μm pitch surface relief gratings induced on SU 8 films is represented in Fig. 4. The modulation depth variation from about 10 nm to hundreds of nanometers evidences the possibility to obtain structures with a large scale of parameters if we know and control the irradiation conditions. Similar dependencies have been obtained also for the interferometric fields of the 355 nm laser radiation.



a)



b)

Fig. 4 – Single step surface relief gratings (1 µm pitch) induced on photoresist film modulation depth dependence on subsequent irradiation pulses number for two fixed incident fluences; incident wavelength = 193 nm, film thickness: a) 2 µm (▲), 1.5 µm (■) and 1.2 µm (●); b) 2 µm (▲), 1.5 µm (●), 1.2 µm (■).

The parameters of the induced surface structure depend on the structure of irradiation light field. For a more complex fluence distribution in the irradiation field it is possible to obtain more complex structures (Fig. 5).

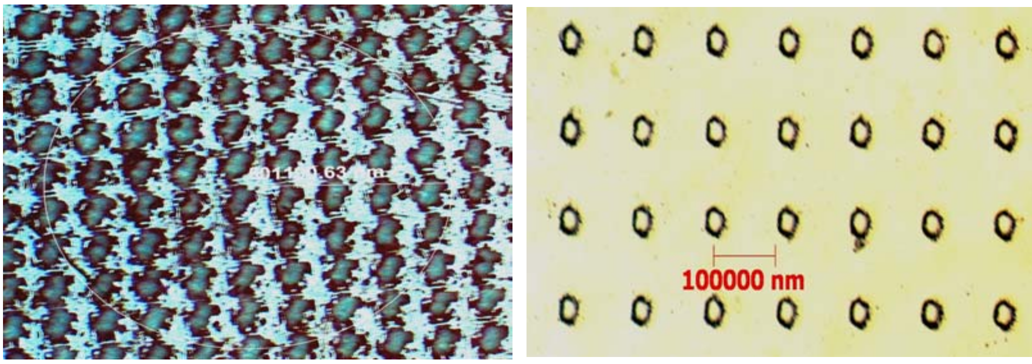


Fig. 5 – Surface relief structures induced on the photoresist film surface under the action of 355 nm laser light field.

3. EXPERIMENTAL GEOMETRY AND DIFFRACTION PROBLEM

The experimental geometry and the diffraction problem are illustrated in Fig. 6. The -1^{st} order is suppressed so that only the 0^{th} and the $+1^{st}$ orders contribute to the formation of the SRG.

The light intensity distribution in the irradiation area was analysed in order to evaluate the photoinduced surface modulation correlation with the incident light field. There were calculated the interference fields for various small values of the distances from the phase mask (in the order of hundreds of microns). The scalar value of the three diffracted fields at a distance *z* from the phase grating may be written as:

$$E_0\left(x,z\right)=E_0^0\exp\left(-\mathrm{i}kz+\mathrm{i}\phi_0\right), \tag{1a}$$

$$E_1\left(x,z\right)=E_1^0\exp\left(\mathrm{i}k\sin\theta_1\quad x-\mathrm{i}k\cos\theta_1 z+\mathrm{i}\phi_1\right), \tag{1b}$$

where E_0^0 and E_1^0 are the real amplitudes of the vector fields $\mathbf{E_0}$ and $\mathbf{E_1}$ and $k=2\pi/\lambda$ is the scalar value of the wavevector. Since the actual phases are arbitrary and only the phases relative to one that is chosen to be the reference are meaningful, we may chose $\phi_0 = 0$ and replace ϕ_1 by $\phi_1-\phi_0$, which we will denote with $\Delta\phi_1$. The interference figures at a distance *z* from the grating is obtained by

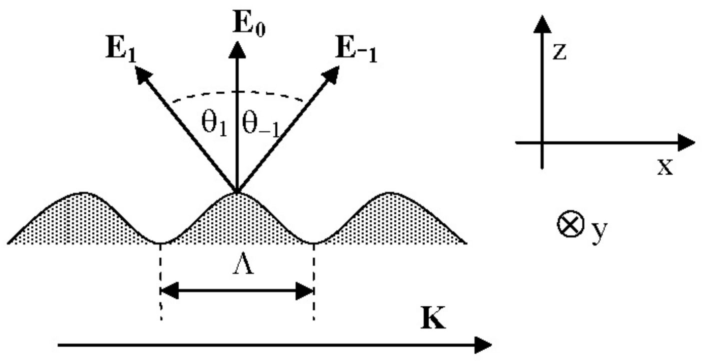


Fig. 6 –Experimental geometry and diffraction problem. The phase grating and the transmitted orders. **K** is the grating vector indicating the direction of periodicity and having the scalar value of $2\pi/\Lambda$. $\theta_{\pm 1} = \pm 11.13°$. The -1^{st} order is suppressed so that only the 0^{th} and the $+1^{st}$ orders contribute to the formation of the SRG.

squaring the absolute value of sum of the transmitted fields:

$$I(x,z) = I_0 + I_1 + 2(I_0 I_1)^{1/2}\cos\left[\Delta\phi_1 + k\ \ (1-\cos\theta_1)z + k\sin\theta_1 x\right]. \qquad (2)$$

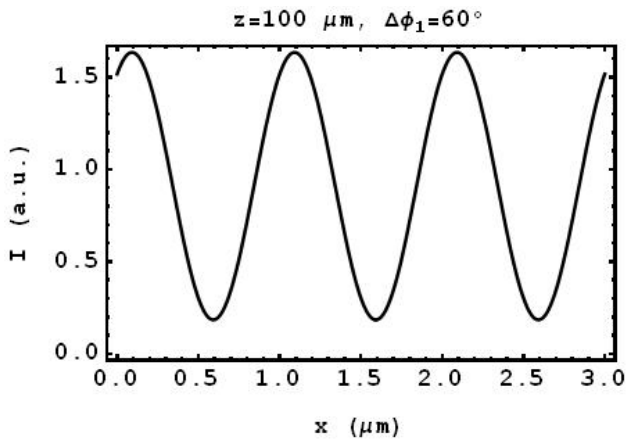


Fig. 7 – Interference sinusoidal pattern calculated for the 1 μm pitch phase grating. The pattern does not depend on the distance *z* from the grating (as long as the distance is small enough) except for a phase shift of the sinusoid, which cannot be measured. The value of the $\Delta\phi_1$ phase shift between the 0^{th} and the 1^{st} orders is also inconsequential.

Formula (2) is illustrated in Fig. 7. The light intensity distributions in the fringe pattern are completely similar for the considered distances.

A comparison of the light intensity distribution in the calculated interference field (Fig. 7) with the AFM profiles of the induced surface relief gratings evidences the fact that the form of the surface induced profiles depends on the incident light field structure. The amplitude of the modulation depth depends on the local fluence and the subsequent pulse number.

4. CONCLUSIONS

The gratings on the photo-resist surface was obtained after laser irradiation at 193 nm (7 ns pulse length) and 355 nm (6 ns pulse length) irradiation through a phase mask with 1090 and 250 nm period. The pitch of the induced surface relief gratings reproduces the pitch of the irradiation interferometric field. The amplitude of the modulation depth was varied from about 10 nm to hundreds of nanometers as a function of irradiation conditions. The laser intensity distribution in the irradiation area was analysed in order to estimate the real fluence thresholds as compared with the measured medium incident fluence to evaluate the photoinduced surface modulation.

The laser fluence used to print the surface structure is less than the ablation threshold of the material and as a result the surface structure is a continuous one. We have evidenced material surface structuration takes place by surface relief modulation and evolution (from disorder to order) as a function of the irradiation pulse number.

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