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Perspectives for using technology of laser thermolithography

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Abstract. Analyzed in this work are the requirements to an optical system for laser thermolithographic recording. It has been shown that possibilities of this type recording with decreasing the registered element sizes can be realized only when using special measures for stabilizing both exposing radiation power and duration of laser pulses. Using the thermolithographic method for making super-dense patterns also requires creation of a specific system for dynamic focusing with accuracy better than 100 nm. It has been shown that the specific heat of thermochemical reaction and thermal resistance of a substrate are critical parameters for this method.

Keywords: thermolithography, laser recording, threshold exposure characteristic.

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1. Introduction

Widely used in the systems for laser recording are photosensitive materials with threshold exposure characteristic to decrease the size of patterns on surface of these materials. Using such materials enables to record elements with sizes 5 to 6 times less than the sizes of irradiated area [1, 2]. The idea to use photosensitive materials with nonlinear exposure characteristic was offered in the early 70s last century [3, 4]. It was also shown then that the recording process in these materials, when obtaining patterns with sizes smaller than the exposing beam diameter, is very sensitive to exposure variations [3, 4].

For a long time, the resolving power of diffraction-limited optical focusing systems was sufficient to record data with a necessary density. Requirements to considerable enhancement of the registration density of optical carriers (transfer to the Blu-Ray format) cause necessity to use the process of nonlinear exposure applied to master-disc photo-sensitive material. Usage of nonlinear processes both for exposure of these materials and processing photoresists enables to decrease the size of pattern elements on substrate surfaces. The main technical problem in using these methods is essential growth of requirements to accuracy of thermoresist exposure.

Up to date, there accumulated is a considerable experimental data concerning usage of the thermolithographic laser recording information and synthesis of thermo-sensitive materials, therefore it is necessary to determine areas for efficient using the thermolithographic methods in application to manufacturing master-discs in newly formats.

2. Analysis of sensitivity of the pattern diameter to changes in the intensity and duration of the laser radiation pulse in the process of thermolithographic recording

Laser thermolithographic recording is provided by exposure of photo-sensitive material with a beam that possesses a non-homogeneous distribution of intensity. More often, light beams with the Gauss distribution of intensity are used in practice. Decreasing the sizes of patterns is possible under conditions of availability of a threshold exposure characteristic of photo-sensitive material and recording process should run in the adiabatic mode. Adiabaticity of the recording process can be provided by using materials with low heat and temperature conductivities, recording process being realized with short laser pulses of 10 to 20 ns duration. The scheme of laser lithographic recording is represented in Fig. 1.

As recording is realized in a layer of threshold photoresist, then the formula to define the pattern radius can be written in the form

$$\beta I_0 T \exp(-r^2/r_0^2) = E_{por}, \quad (1)$$

where T is duration of the recording pulse, E_{por} - threshold energy, I_0 – light intensity in the center of laser spot on photoresist surface, β - absorption coefficient for electromagnetic energy absorbed in the photoresist layer. When the laser radiation intensity is changed, the change in radius of pattern (i.e., the pit width) can be found from the condition of shifting the threshold energy contour for this new intensity value in the laser spot

$$T\delta\left(I_0 \exp(-r_p^2/r_0^2)\right) = \delta E_{por} = 0 \quad (2)$$

$$\delta I_0 \exp(-r_p^2/r_0^2) - \\ - \exp(-r_p^2/r_0^2) I_0 2r_p \delta r_p / r_0^2 = 0 \quad (3)$$

$$\delta I_0 - I_0 2r_p \delta r_p / r_0^2 = 0 \quad (4)$$

$$\frac{r_0^2}{2r_p^2} = \frac{\delta r_p / r_p}{\delta I_0 / I_0} \quad (5)$$

Putting the pit diameter as $w = 2r_p$ and beam diameter (i.e., the diameter where the beam intensity is decreased by e times) $D = 2r_0$, the equation can be re-written as

$$\frac{D^2}{2w^2} = \frac{\delta w / w}{\delta I_0 / I_0}, \quad (6)$$

which can be given in the following form

$$\frac{\delta w / w}{\delta I_0 / I_0} = \frac{D^2}{2w^2} \quad . \quad (7)$$

To take into account the pulse duration (time interval), it is necessary to differentiate the formula (1) under condition that the laser beam intensity is constant

$$I_0\delta\left(T \exp(-r_p^2/r_0^2)\right) = I_0\left(\delta T \exp(-r_p^2/r_0^2) - \\ - \exp(-r_p^2/r_0^2) T 2r_p \delta r_p / r_0^2\right) = \delta E_{por} = 0 \quad (8)$$

After transformations similar to that made in the formulae (4) to (6), we obtain the ratio of the normalized pit width to the normalized laser pulse duration

$$\frac{\delta w / w}{\delta T / T} = \frac{D^2}{2w^2} \quad (9)$$

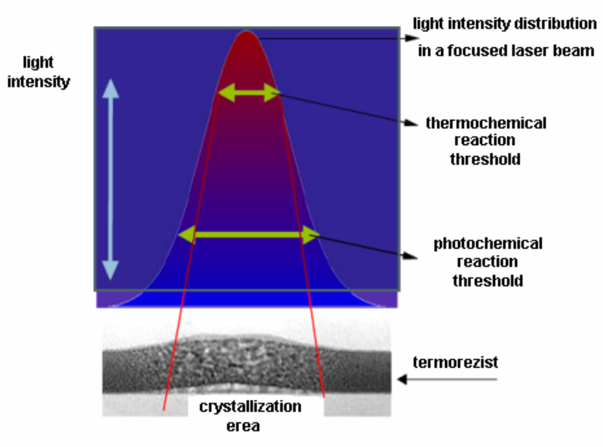

Fig. 1. Distribution of the laser radiation intensity in the process of thermolithographic recording.

Thus, the formulae of sensitivity for the pit width to the intensity of laser radiation as well as to pulse duration are identical. It means that, during information recording in the regime when this recording is performed in a narrow area near the beam center, sensitivity of the relative pit diameter to changes in the intensity and pulse duration will grow in inverse proportion to the pit diameter. While the absolute pit changes will be in proportion to the inverse pit diameter.

Depicted in Fig. 2 is the dependence of relative changes in the pattern diameter on relative changes in the power of exposing laser radiation, where dashed lines indicate the operation regimes that correspond to recording DVD master-discs. Tables 1 and 2 contain values of the sensitivity of pit width for DVD and BD master-discs to changes in the intensity of laser beam field for lasers with different light wavelengths and for usage of objectives with different numerical apertures.

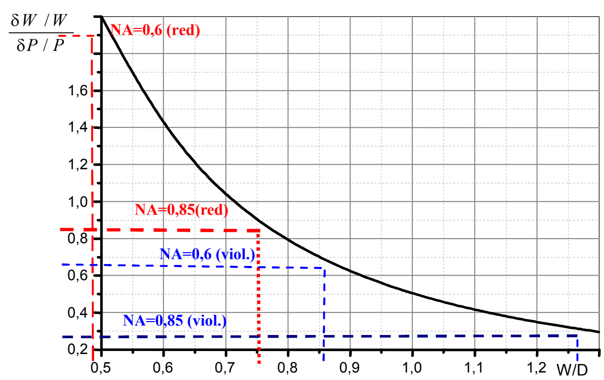

Fig. 2. Dependence of relative changes in the pattern diameter on relative changes in the power of exposing radiation for ROM DVD.

Table 1. Sensitivity of changes in the pit width for DVD master-discs to changes in the radiation intensity (exposure time) of red and violet laser diodes.

NA	D, μm λ=0.65 μm	D, μm λ=0.405 μm	W/D λ =0.65 μm	W/D λ=0.405 μm	$\frac{\delta w/w}{\delta I/I}\left(\frac{\delta w/w}{\delta T/T}\right)$ λ =0.65 μm	$\frac{\delta w/w}{\delta I/I}\left(\frac{\delta w/w}{\delta T/T}\right)$ λ=0.405 μm
0.6	0.574	0.358	0.55	0.89	1.65	0.63
0.85	0.405	0.252	0.79	1.27	0.80	0.31

Table 2. Sensitivity of changes in the pit width for Blu-Ray master-discs to changes in the radiation intensity (exposure time) of red and violet laser diodes.

NA	D, μm λ=0.65 μm	D, μm λ=0.405 μm	W/D λ=0.65 μm	W/D λ=0.405 μm	$\frac{\delta w/w}{\delta I/I}\left(\frac{\delta w/w}{\delta T/T}\right)$ λ=0.65 μm	$\frac{\delta w/w}{\delta I/I}\left(\frac{\delta w/w}{\delta T/T}\right)$ λ=0.405 μm
0.6	0.574	0.36	0.23	0.36	9.75	3.8
0.85	0.405	0.25	0.32	0.52	4.9	1.9

As can be seen from the adduced plots and tables, recording the master-discs in DVD format by using radiation with the wavelength 405 nm and objectives with the apertures o.6 and 0.85 takes place in the regime when relative variations of the laser radiation power are less than relative variations of the pattern diameter on the carrier surface and relative exposure time. In the case of BD, sensitivity of pattern sizes to the laser radiation intensity and exposure time is approximately 6-fold increased, and variation of the pattern size exceeds variations of relative intensity (exposure time) approximately twice even when using violet laser and objective with a maximum numeric aperture.

Using radiation with the wavelength 0.65 μm in the thermolithographic regime for recording information on master-discs in DVD and BD formats seems unreasonable in relation with considerable variations of pattern sizes under changing powers of exposing radiation.

Also, the represented data show that information recording on master-discs in BD format by using radiation with the wavelength 405 nm and high-aperture optics (A = 0.850) requires application of special stabilization systems for the laser radiation power.

It should be noted that the above obtained estimates of sensitivity are somewhat understated, since they do not take into account heat transfer from the central part of the light spot to periphery in the course of heating and thermal reaction, which inevitably should result in increase of the pattern sizes.

3. Influence of thermal conduction and specific heat of thermochemical reaction on pattern sizes.

When recording information on an optical disc, heating the registering layer occurs in accord to distribution of the laser beam intensity. Since recording occurs not instantaneously but for definite time interval, and absorption of light energy takes place in the course of the very recording process (i.e., during the thermochemical reaction), then due to thermal conduction a part of energy from the spot central area is transferred to periphery. Let us make an estimate of the thermal conduction effect on the pit size for the case when the thermal energy from the registering layer does not channel off to the substrate or neighboring layers. Valid in this case is the two-dimensional model of heat propagation. In this model, thermal energy propagates from the center of light spot to its periphery. Let us consider that this light spot possesses the Gauss distribution of light intensity with the center in the origin of coordinates $I(x) = I_0 \exp\left(-x^2/r_0^{\,2}\right)$. In this case, changes in temperature are described by the following equation in partial derivatives:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{\eta I(x)}{c_p \rho}, \qquad (11)$$

where $\alpha = \frac{k}{c_p \rho}$ is the coefficient of thermal diffusion, η - coefficient of light absorption, c_p - thermal capacity, ρ - mass density. A solution of this equation can be written through the integral of Green's function

$$T(x,t) = T_0 + \frac{1}{c_p \rho} \int_0^t \int_{-\infty}^{\infty} G_T(x,x',t,t') q(x',t') dx' dt', \qquad (12)$$

where $G_T(x,x',t,t') = \sqrt{\frac{1}{4\pi\alpha(t-t')}} \exp\left(-\frac{(x-x')^2}{4\alpha(t-t')}\right)$ is the Green function for the diffusion equation

$$T(x,t) = T_0 + \frac{2\sqrt{\pi}\eta I_0}{R c_p \rho} \exp\left(-\frac{x^2}{r_0^{\,2}}\right) \times$$
$$\times \int_0^t \left(1 - \frac{2\alpha(t-t')}{r_0^{\,2}}\right) \exp\left(\frac{4\alpha(t-t')x^2}{r_0^{\,4}}\right) dt' \qquad (13)$$

If the light pulse is short ($\frac{\alpha t}{r_0^2} << 1$), after some transformations the formula (13) can be simplified (with the accuracy $\left(\frac{t\alpha}{r_0^2}\right)^2$) as follows:

$$T(r,t) = \frac{2\sqrt{\pi}\eta I_0}{r_0 c_p \rho} \exp\left(-\frac{r^2}{r_0^2}\right) t \left(1 + \left(1/2 + r^2/r_0^2\right)\frac{\alpha t}{r_0^2}\right). \quad (14)$$

That is the temperature profile will differ from the beam intensity profile by a small value

$$\delta T / T = \left(1/2 + r^2/r_0^2\right)\frac{\alpha t}{r_0^2}. \quad (15)$$

Thus, in order that the heat transfer does not increase the pattern size, the exposure time should satisfy the following inequality

$t << r_0^2/\alpha$

Let us estimate a maximum possible exposure time value for the case when the heat transfer does not create considerable problems (without account of thermal processes related with the thermochemical reaction itself) for manufacturing BD by using the chalcogenide layer of $Ge_2Sb_2Te_5$ as a thermoresist

$$t << r_0^2/\alpha =_0^2 /(k/(c_p\rho)) \times$$

$$\times \frac{\left(1{,}30 * 10^{-7}\right)^2}{0{,}5/(4{,}83*10^3 * 1{,}25*10^6)} = 2{,}03*10^{-4}\, c,$$

where values of physical parameters were taken from [5-7].

However, temperature distribution will be essentially differ from intensity distribution for electromagnetic field in the case when the process of thermochemical reaction requires absorption (endothermic process) or emission (exothermic process) of a considerable heat amount. In the case of exothermic reaction, inside the area where the critical threshold of reaction is already reached, to support this reaction it is necessary to provide this area with an additional energy to complete transformation of the registering layer in this part. During the thermochemical reaction, neighboring parts of thermoresist surface will be heated. As a consequence, in these parts of thermoresist the temperature threshold can be overcome, too, and partial transformation of the registering layer can be realized there. It means creation of the intermediate range where the recording reaction is not completed. The higher the specific energy for thermochemical reaction, the longer time is necessary for full completion of the reaction and the larger part of neighboring thermoresist range can be heated above the threshold temperature. As a first approximation, we shall assume that, after reaching the threshold temperature in the periphery part of the pattern, the reaction runs quickly, and heat transfer due to thermal conduction can be neglected. The intermediate range where the recording reaction is not fully completed can be defined as the range between the surface where the reaction is completed and the contour within which the critical temperature was reached only at the end of recording. The equation for the size of range with partial transformation of thermoresist can be written as follows

$$\eta I_0 \exp\left(-\left(r/r_0\right)^2\right)\Delta t/\rho\Delta Q =$$

$$= \eta I_0 \exp\left(-\left((r+\Delta r)/r_0\right)^2\right)\Delta t / \quad (16)$$

$$\left(c_p\rho\left(\Delta T_{kr} - \Delta T_{kr}\exp\left(-\left((r+\Delta r)/r_0\right)^2\right)\right)\exp\left(\left(r/r_0\right)^2\right)\right),$$

where ΔQ is the specific heat of reaction, $\Delta T_{kr} = T_{kr} - T_0$, T_0 and T_{kr} are initial and threshold temperatures, respectively, ρ is the mass density of the registering layer, c_p - specific heat capacity, Δt - time interval, r - radius of the surface where all material reacted, Δr - width of the intermediate range ring. Eq. (16) enables to obtain the formula for the range width Δr:

$$\frac{\Delta r}{r} = \frac{\frac{r_0}{r}\frac{\Delta Q}{c_p\Delta T_{kr}}}{\sqrt{\frac{\Delta Q}{c_p\Delta T_{kr}} + \left(r/r_0\right)^2} + r/r_0} \quad (17)$$

In the case of optical recording, the pit radius is approximately equal $r_p = r + \Delta r/2$. It implies that for obtaining the pits with small radii the width of the intermediate range should be considerably less than the area of full transformation. It follows from the equation (17) that the condition of small width for the intermediate range ($\Delta r/r << 1$) needs fulfillment of the following inequality

$$\frac{\Delta Q}{c_p\Delta T_{kr}} < \left(r/r_0\right)^2, \quad (18)$$

which means that the specific heat of reaction should be insignificant ($\Delta Q << c_p\Delta T_{kr}$).

The analysis of the exothermic reaction results in the same conclusion. As the condition of a small value for the reaction heat ($\frac{\Delta Q}{c_p\Delta T_{kr}}$ >1) is not valid for many materials (Ge_2Sb_2 Te_4 is a typical example), a decrease in the width of intermediate range can be reached by choosing some additional layers with a necessary thermal conduction as well as intensity and duration of laser pulses. In this case, the latter parameter should be of the order of 10 ns. Thus, it is the reaction heat that critically influences on temperature distribution in thermo-photo-resist, which requires application of nanosecond pulses. Therefore, when using thermoresists for super-dense recording, one of the main criteria for choosing materials should be the value of the specific heat inherent to the thermochemical reaction.

It follows from the analysis made in this paragraph that the estimates made in the previous paragraph for sensitivity of pit sizes to variations of the intensity and duration of laser pulses provide only lowered values of sensitivity. Under real recording, with account of heat transfer processes as well as emission or absorption of heat in the recording reaction, sensitivity of pit sizes to the intensity and duration of light pulses will be essentially higher than the values obtained in the previous paragraph.

4. Analysis of thermolithographic recording the data on master-discs in BD format

In recent years, interest to thermolithographic methods for recording is related with the necessity to record information on master-discs in BD format by using the traditional diffraction-limited optical systems. The optical-and-mechanical system as well as electronics for thermolithographic recording are similar to those used in BD drives. For these purposes, one can use the well-developed for optical recording methods of multi-pulse recording aimed at optimization of the very method and enhancing reliability of optical recording. The process of information recording is accompanied by changes in optical properties of thermoresist. Therefore, one can observe changes in the reflective ability within the illuminated area and use it for working out the optimal conditions for recording without using all the following processes aimed at creation of master-discs. The systems for thermolithographic recording possess small sizes, are light-weight, reliable and stable, have low power consumption. Besides, they need not water cooling. These systems can provide the high recording velocity (10 Mb/s) and do not require application of complex vacuum systems.

The process of thermolithographic recording the master-discs is influenced by variations of the recording laser power and duration of laser pulses as well as beats of the information carrier surface, which are not compensated by the system for automated focusing.

The highest influence on the process of thermolithographic recording the master-discs is done by the operation accuracy of the system for automated focusing. When recording the master-discs in BD format, variation in pattern sizes should not exceed 15 nm. This requirement leads to condition that exposure variations should not exceed 7 %. As the duration of one pulse is approximately 10 ns, it should be kept with the accuracy not worse than 0.7 ns.

Investigations of accuracy in focusing the light spot on surface of threshold thermoresist for recording the master-discs in BD format were performed by us in previous works [8-9]. It was shown there that precision of focusing should be not worse than 40 – 80 nm (in dependence of peculiarities inherent to the used optical head objective). Therefore, uncompensated beats of master-disc surface should be less than 40 – 80 nm.

5. Conclusions

1. Usage of the thermolithographic method for recording information on master-discs in BD format requires application of special high-precision systems for stabilizing the power of exposing laser radiation as well as duration of laser pulses.
2. The thermolithographic layer should possess a low specific heat of reaction as compared with the heat necessary to rise the thermoresist temperature up to the threshold one.
3. The substrate should have a necessary thermal resistance able to provide a needed velocity of heat drain from the thermoresist layer.

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