Local Laser Oxidation of Thin Metal Films: Ultra-resolution in Theory and in Practice

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Laser–induced oxidation on thin metallic films with following selective etching is a powerful method for micropatterning of different structures like photomasks, diffractive optical elements etc.Nowadays the most interesting question is how small could be structures produced by this technology, what are theoretical limitations and where is a practical limit for that? Under this research will be shown that Arrhenius dependence of oxidation speed from temperature raises this limit on some orders of magnitude higher then the resolution of thermal image. Corresponding calculation will be done and will be verified experimentally. From the other hand régimes of laser irradiation (power density, time of irradiation etc) as well as régimes of selective etching (type of etchant and its concentration), material of thin film and its thickness have also big influence on the final results. Experimental and practical results for fabrication of many specific components and devices as different diffraction lenses, diffraction attenuators, synthesized holograms will be demonstrated.

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1. Introduction

In optics science there is a class of optical elements that have very complex topology structures, based on thin metal films (TMF) deposited on dielectric (commonly glass) substrate. First of all we can name in this class diffractive optical elements (DOE) those are used for geometrical and wave transformation of light beams diffracting on theirs structure [1].

At the present moment DOE are widely implemented in various applications like printers, cash registers, devices for reading bar code, laser CD or DVD players, etc. New types of DOE are implemented in technological systems, laser scalpels, artificial crystalline lenses, and so on.

In recent years accuracy of DOE increased very much that allows to solve very difficult problems – construction of wavefront correctors (zero lens) that can form reference wavefronts used for control of aspheric optics – main mirrors of modern telescopes.

Spatially structured thin film elements on transparent substrates underlie optical memory devices, sound and video-recording (OR) [2].

Finally, precision technological instrument in microelectronics – photomask (PM) – can be referred to this class.

In all of these cases we talk about finely structured non-transparent TMF on transparent substrate (in most cases TMF is chrome). Type of absolute contrast structure – annular (DOE), spiral (optical data recording), rectangular-random (PM) – defines the purpose and application field of these elements. Technological principles of forming elements are lying in their foundation, and basic requirement for them is high resolution. Increase of resolution capability ensure development of microelectronics and optics, and allow us to find and solve new classes of problems [4].

Laser lithography in our days is the best way of DOE, OR, and PM topology formation. In most cases it is based on traditional photolithography (PL) with laser exposition of photoresist [5]. But because of its complexity and time-consuming nature everybody wants to find another method of topology formation.

One of these methods is laser evaporation of TMF, but it has some limitations in accuracy and quality of topology structures due to thermal and hydrodynamic aberrations in image [6].

One of the most perspective methods is laser thermochemical method (LTM) based on local laser oxidation (LO) of TMF with subsequent etching of non-irradiated areas [7].

By the means of this method recently very interesting results were obtained [1]. But till this time no one can point its limits in resolution capability, and this obstacle restricts the range of applications for this method.

Aim of this article is to make theoretical analysis of resolution capabilities of LTM with LO and its comparison with experimentally obtained results. Making this research we stated that the most developed field of LTM practical implementation is production of DOE [1]. Annular structures are topological feature of DOE that is why all experiments were conducted on laser generator of annular structures, developed in Institute of automatics and electrometry, Siberian department of RAS, [1]. In accordance with this for better and specific comparison with experiment there was developed a physico-mathematical model of local surface oxidation of chromium thin film by the means of laser scanning beam with continuous laser radiation that has small sized cross-section and Gaussian distribution of intensity. It is shown that sharp dependence between thickness of oxide layer and temperature results in layer thickness gradients exceeding the temperature gradients. Possibilities of producing diverse submicron structures with size d smaller than diameter of laser beam d_0,

and radiation wavelength λ, on thin films are shown. Situation when d is smaller than λ we call ultra-resolution.

2. Problem definition

Let us consider oxidation of chromium thin film on the K-8 glass substrate. Oxidation process is induced by focused on the surface of the thin film scanning beam of continuous laser radiation. Some part of laser radiation that reaches the surface is being reflected from it and some part is being absorbed by the material. Influence on every point lasts for some period of time. This period of time depends on diameter of laser beam and scanning speed. The time pulse shape that affect every definite point on surface depends on spatial intensity distribution of laser beam. Absorption of radiation results in heating of the thin film directly under the focused laser beam and in the neighborhood. Heating of the film activates several physicochemical processes, like surface adsorption of oxygen, diffusion and electron transport of metal and oxygen ions, chemical oxidation of metal with oxide layer formation, and others [8]. Definite relation between oxide layer thickness H and temperature T is determined by the ratio of the above mentioned processes rates. The most frequently encountered law is Wagner oxidation law, according to which:

$$\frac{dH}{dt} = \frac{B}{H}\exp\left(-\frac{T_a}{T}\right) \tag{1}$$

where B – parabolic oxidation constant, T_a - activation energy of diffusion processes, in Kelvin, and t – current moment of time.

For evaluation of oxide layer thickness in the case of nonisothermal oxidation let's use method, developed by Libenson M.N. [3]: as far as the temperature of thin film is substantially smaller than T_a, then exponential curve of activation sharply increases with the growth of temperature, and main contribution in increasing of oxide film thickness is made by those moments, when temperature T is close to its maximum value $T_{\max}$. Considering this we can evaluate thickness of oxide layer under laser (nonisothermal) heating as equivalent to thickness of oxide layer under isothermal heating during some definite equivalent time period (shorter than time of laser radiation influence) t_e:

$$H = \sqrt{2B\exp\left(-\frac{T_a}{T_{\max}}\right)t_e} \tag{2}$$

Value of t_e is determined by the pattern of temperature change with time under laser treatment. Particularly if temperature maximum is being reached in some moment of time t_0 during laser treatment, then [2]

$$t_e = \sqrt{\frac{2\pi T_{\max}^2}{T_a\left|T_{tt}''(t_0)\right|}} \tag{3}$$

Thus, definition of relation between temperature of film and time in every point of film make it possible to determine the structure of generated oxide.

Subsequent etching forms the topology by deleting parts of film that are not covered with oxide layer of sufficient thickness. Critical value of this thickness is not determined exactly yet. In different sources this value is estimated in range from 4 to 8 nm. In evaluation procedure of upper limit of minimal element thickness in film layer, obtained by the use of laser oxidation, we have used value 8 nm.

3. Calculation of oxide layer thickness under scanning beam of continuous laser radiation

Let us consider heating of metallic film with thickness h on a dielectric substrate. Heating process is induced by scanning beam of continuous laser radiation. Let us consider quasi stationary heating regime. We have made preliminary assessment calculation of relation between heat flows from irradiated region to the film P_1 and to the substrate P_2:

$$\frac{P_1}{P_2} = \frac{2h}{r_0}\sqrt{\frac{a}{a_s}} \tag{4}$$

where r_0 - radius of laser beam, a – film thermal diffusivity, a_s - substrate thermal diffusivity. In the majority of cases important in practice: $P_1/P_2 > 1$, particularly, for chrome film with thickness 100 nm on a K-8 glass substrate, and radius of irradiated area 0.25 μm, $P_1/P_2 \approx 4$.

Considering this we will regard film, heated by the laser radiation, as adiabatically isolated film, and neglect the heat sink to the substrate.

Heat conduction equation for the film is:

$$\frac{\partial T}{\partial t} - a\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}\right) = \frac{P(1-R)}{\pi r_0^2 \rho c h}\exp\left[-\frac{(x-Vt)^2 + y^2}{r_0^2}\right] \tag{5}$$

where P – laser output power, T – film temperature, ρ - film density, c – heat capacity of film, V – scanning speed, R – reflection coefficient of film, r_0 - characteristic value of Gaussian intensity distribution in beam, t – current moment of time. Axes x and y lay on the plane of the film surface, and x-axis coincide with direction of scanning and crosses the center of irradiated area, y-axis is perpendicular to x-axis.

Let us pass over to moving coordinate system connected with irradiated area. Heat conduction equation is:

$$\frac{\partial^2 T}{\partial z^2} + \frac{\partial^2 T}{\partial y^2} + \frac{V}{a}\frac{\partial T}{\partial z} + \frac{P(1-R)}{\pi r_0^2 k h}\exp\left(-\frac{z^2 + y^2}{r_0^2}\right) = 0 \tag{6}$$

where $z = x - Vt$, k – film heat conduction.

Changing the variables

$$T = e^{-\frac{Vz}{2a}} f(y,z), r = \sqrt{\left(z - \frac{Vr_0^2}{4a}\right)^2 + y^2} = \\ = \sqrt{\left(x - Vt - \frac{Vr_0^2}{4a}\right)^2 + y^2} \tag{7}$$

we will transform equation (6) to:

$$\frac{d^2 f}{dr^2} + \frac{1}{r}\frac{df}{dr} - \frac{V^2}{4a^2}f + \frac{P(1-R)}{\pi r_0^2 k h}e^{\left(\frac{Vr_0}{4a}\right)^2} e^{-\left(\frac{r}{r_0}\right)^2} = 0 \tag{8}$$

Using zero-order Hankel transform to solve equation (8) we'll get final expression for temperature of film:

$$T = G\int_0^\infty \frac{\xi}{\xi^2 + b^2} e^{-\frac{\xi^2}{4}} \mathrm{J}_0\left(\xi\frac{r}{r_0}\right) d\xi \tag{9}$$

where $G = \frac{P(1-R)}{2\pi kh} e^{\frac{b^2}{4}}$, $b = \frac{Vr_0}{2a}$, $J_0(u)$ - first-type Bessel function of zero-order, value of temperature is counted from its initial value.

Value of derivative of temperature with respect to time is $\frac{\partial T}{\partial t} = \frac{\partial T}{\partial r}\frac{\partial r}{\partial t}$, where $\frac{\partial r}{\partial t}$ is calculated from equation (7). Calculations show maximum temperature $\frac{\partial T}{\partial t} = 0$ in points $r = y$.

In the same way we can find the second derivative: $\frac{\partial^2 T}{\partial t^2} = \frac{\partial}{\partial r}\left(\frac{\partial T}{\partial t}\right)\frac{\partial r}{\partial t}$. For $r = y$

$$\frac{\partial^2 T}{\partial t^2} = -\frac{GV^2}{r_0}\int_0^{\infty} \frac{\xi^2}{\xi^2 + b^2} e^{-\frac{\xi^2}{4}} \frac{J_1\left(\xi \frac{y}{r_0}\right)}{y} d\xi \qquad (10)$$

where $J_1(u)$ - first-type Bessel function of first-order.

For simplification of subsequent calculations for determination of temperature and its second time derivative we have used expansion of Bessel function into a series:

$$T = \frac{G}{2}\left[\exp\left(\frac{b^2}{4}\right)E_1\left(\frac{b^2}{4}\right) + \sum_{n=1}^{\infty}\frac{(-1)^n}{nn!}\left(\frac{y}{r_0}\right)^{2n}\right] \approx$$
$$\approx \frac{G}{2}\left[-\gamma - \ln\left(\frac{b^2}{4}\right) + \sum_{n=1}^{\infty}\frac{(-1)^n}{nn!}\left(\frac{y}{r_0}\right)^{2n}\right] \qquad (11)$$

where $E_1(u)$ - integral exponential function, $\gamma = 0.5772156$ - Euler constant.

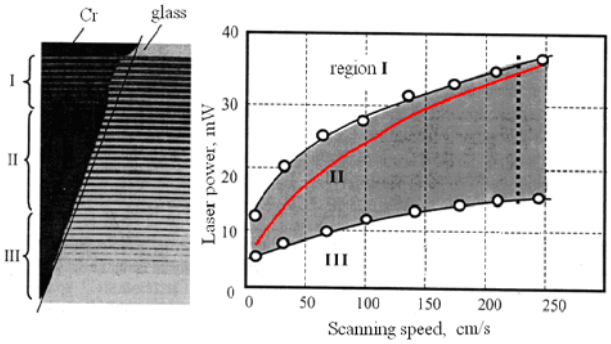
$$\frac{\partial^2 T}{\partial t^2} = -\frac{GV^2}{r_0}\sum_{n=0}^{\infty}\frac{(-1)^n}{(n+1)!}\left(\frac{y}{r_0}\right)^{2n} \qquad (12)$$

4. Calculation results

Calculations show that laser power needed for thermochemical machining of 100 nm chrome film lies in the range from 10 to 20 mW for 10-100 cm/s scanning speed. These results are in a good agreement with experimental results: 10-30 mW. Power of laser radiation must be changed depending on scanning speed in such a range, where from one side thickness of the film exceed the critical value, and from another side there is no melting.

Admitted region of laser power output depending on scanning speed theoretically calculated and in experiment is demonstrated on Fig. 1. It is experimentally shown, that for different values of laser power and scanning speed there are three following regimes: I is region of film melting, II is working regimes region, III is region of insufficient laser heating of the film for oxide layer formation. Red-colored curve is theoretically calculated threshold (boundary of the II and III regions).

Calculations showed that reduction of oxide layer thickness from the center of the laser spot (perpendicular to the direction of scanning beam) occurs much faster than reduction of maximum temperature (Fig. 2). This fact is a premise for obtaining minimal sizes of elements and, therefore, high resolution



a b

Fig. 1. Laser oxidation of 100nm chromium thin film: a – fragment of the series of test lines before and after etching, b - admitted region of laser power output depending on scanning speed.

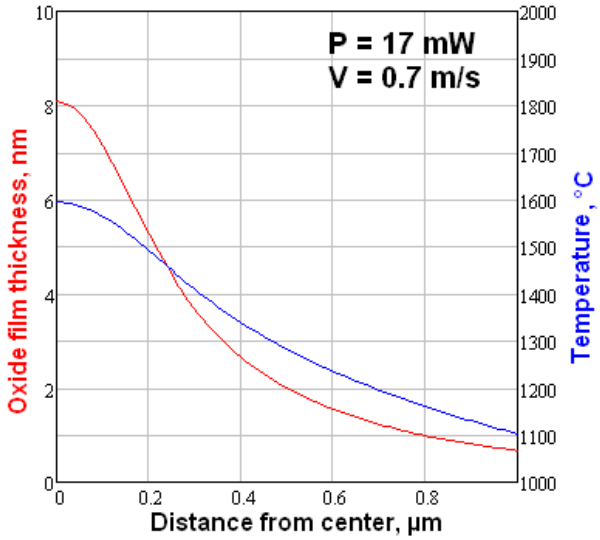


Fig. 2. Calculated dependence between oxide layer thickness, maximum temperature and distance from the center of the laser spot (P = 16.05 W, V = 0.5 m/s, h = 100 nm)

Calculated values of minimal width of obtained pattern (we assumed that critical oxide layer thickness, that corresponds to the edge of pattern, is 6 nm) lies in the range from 0.4 μm at minimum laser power or maximum scanning speed (lower curve on Fig. 1) and to 2.5 μm at the melting threshold (upper curve on Fig. 1), when diameter of laser beam on the surface is 0.5 μm. If value of laser power is selected in the right way – according to scanning speed – then minimal width of obtained pattern practically don't depend on scanning speed. Thereafter value of resolving ability lies in the range between 2500 and 400 mm^{-1}.

5. Experimental results

The investigation of thermochemical ultra-resolution was made using the laser writing system built at the Institute of Automation and Electrometry [4]. The substrate with thin chromium film is fixed on the top of precision air-bearing spindle. Laser power of a 1-W argon laser is controlled

with 10-bit resolution. The laser beam is focused to a 0.6 μm spot (at ½ level) and the focus is held by servo control. The focusing optical system is moved radially using an air bearing stage, linear motor, and interferometric position feedback. The range of stage displacement is 250 mm, the positioning precision is near 20 nm rms, and the positioning resolution is less 1 nm.

At the experiments we used sputtered chromium films with about 70 nm thick evaporated films on fused silica substrates. The recording spot velocity is varied from 4 to 180 cm/s. It corresponds to radii of 0.5 mm to 30 mm at rotation speed about 10 cycles/sec. The exposed films were developed (time is about 3 min) in the selective etchant [10] consisting of 6 parts of 25% solution of $K_3Fe(CN)_6$ and 1 part of 25 % solution of NaOH.

Investigation of exposed patterns was made using optical microscope (INTERFAC) and AFM (SOLVER PRO). Fig. 3 shows the photomicrography (~40x40 μm) of test pattern recorded on the chromium films (20mm radius, 150 cm/s velocity). The line spacing (or tracks) is 1.5 μm. The gap between groups is 1 μm in radial direction. The laser power decreases top-down. The width of recorded tracks is seen to depend linearly on the laser power as shown in Fig. 4. Laser beam power was normalized to maximum required power (P_c – critical power or power of chromium film melting).

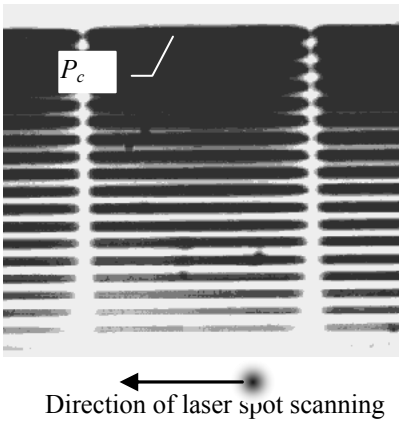


Fig. 3. Photomicrography of test pattern.

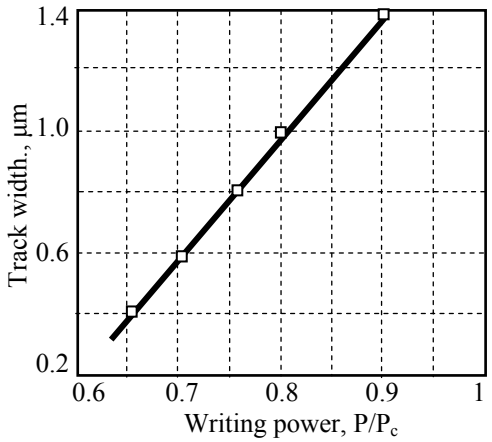


Fig.4. The width of recorded tracks as a function of writing power.

Track profiles (received with AFM) with 0.9μm and 0.4 μm width (at ½ level) are shown in Fig. 5. One can see that track has peakedness (width of 200 nm at 0.7 level) shape at minimum writing power whereas writing spot has near the Gaussian distribution with larger width. This experimental result is confirmed the theoretical result presented in Fig. 2.

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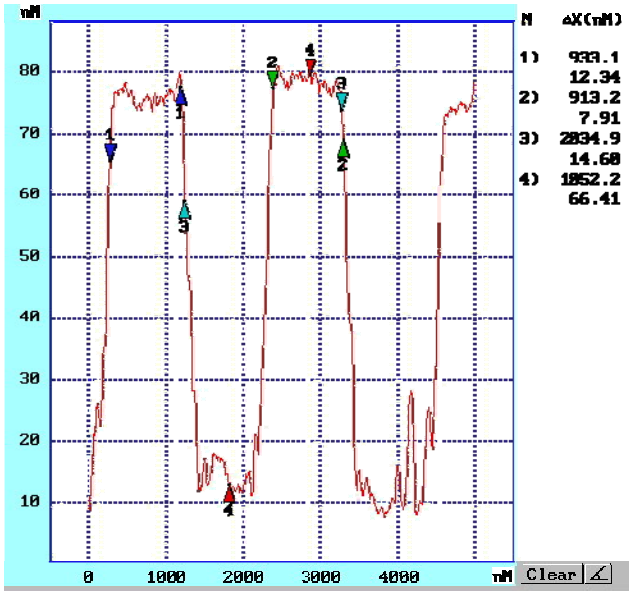
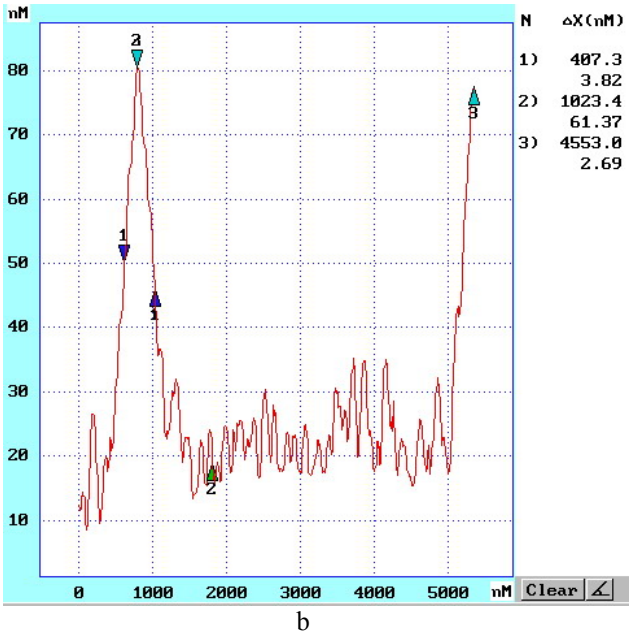


a



b

Fig.5. Chromium track profiles received with AFM. Track width is 0.9 μm (a) and 0.2 μm (b) at 0.7 height level.

6. Conclusions

1. Resolution of thermochemical image is shown to be much higher than that of thermal image due to reverse exponential (Arrenius) dependence of oxide grow speed and thickness on temperature. In this case resolution depends

on relation between the first derivations $\frac{1}{H}\left|\frac{\partial H}{\partial x}\right|$ and $\frac{1}{T}\left|\frac{\partial T}{\partial x}\right|$.

2. Real (experimental) resolution of thermochemical image is even higher due to photo–thermo–chemical feed-back between absorbed power density qA, oxide thickness $H(T)$, and temperature $T(qA)$.

3. Theoretical and experimental limitation on resolution depends on minimal thickness $H_{\min}$ of the oxide resistent to etching, the less are $H_{\min}$, $d_{\min}$, $t_{\min}$, and the higher is the resolution δ.

Actually $H_{\min}$ has an order of magnitude about 1–10 nm which is much less that wavelength λ.

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