Applied Surface Science 278 (2013) 26–32

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Instability-triggered transformations in thin chromium film on glass under laser irradiation

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ARTICLE INFO

Article history:
Available online 29 March 2013

Keywords:
Plateau–Rayleigh instability
Marangoni effect
Capillarity force
Thin chromium film
Self-organization
Laser

ABSTRACT

Metal films on transparent substrates are widely applied for mask production in lithography, and lasers are frequently used for their patterning. Quality of the patterning is limited by fundamental phenomena taking place close to edges of the laser ablated area. We experimentally and numerically investigated transformations in metal films during their irradiation with the nanosecond laser beam with fluences above the ablation threshold. Ridges of the resolidified metal with not uniform thickness were always formed on edges of the cleaned area. Instabilities during the ablation process forced the molten metal in the ridges to break up into droplets with the periodicity predicted by the Plateau–Rayleigh instability. The droplets on ridges were starting points for formation of ripples of metal film by irradiation with partially overlapping laser pulses. The initial droplets and later the self-organized parallel lines of chromium metal were heat sinks that cooled down the metal in their close proximity. Temperature modulation along the laser irradiation spot was high enough to initiate the Marangoni effect which resulted in movement of the molten metal from hot to colder areas.

1. Introduction

Metal films on glass are widely used in industry for diverse applications. The chromium film on glass is an important material in the photo mask production for lithography [1,2], as well as in production of diffraction gratings [3], and linear optical encoders for metrology [4,5]. Lasers are frequently applied for patterning the metal film instead of the wet chemical or plasma etching [6]. When performing micromachining using lasers, multiple bursts of lower power irradiation are employed to minimize heating. However, ripples, or laser-induced periodic surface structures, are observed at intensities near the ablation threshold [7]. Transformation of the metal film structure under laser beam irradiation is in some extend undesirable effect but at same time it is a promising method for micro- and nano-structuring of the functional surfaces [8].

In the previous works, the beam of a nanosecond laser tightly focused to a line was applied for the back-side ablation of the thin chromium film on the glass substrate [9–11]. The stripe-like area ablated with a single laser pulse had cylindrical ridges of the melted metal. The partially overlapping pulses formed a complicated structure made of the metal remaining from the ridges. Regular structures of resolidified chromium metal were formed when laser fluence was above the single-pulse removal threshold and the shift between pulses was less than half width of the stripe ablated with a single laser pulse. The regular ripples were located periodically with the period of 2.5–4 μm. Ripples were orientated perpendicularly to the long axis of the beam spot and their length increased with every shifted pulse. Formation of regular diffraction gratings was experimentally implemented by using the above-mentioned technique [12]. The physical phenomenon responsible for the self-organization of chromium thin film on the glass substrate in to regular structures was still unknown.

In this work, the theoretical model of self-organization of chromium metal thin film in to parallel lines of metal under irradiation by sequence of partially overlapping laser pulses is presented. Plateau–Rayleigh instability in a cylindrical ridge of the molten metal on a rim of the laser ablated area was found to be an initiator at the beginning of the ripple formation. Marangoni (thermocapillarity) flow stabilized the process and led to a steady and regular growth of ripples along the scanning direction by irradiation with partially overlapping laser pulses. The thermal gradient of the surface tension pushes molten chromium from hotter to colder areas stabilizing the process of regular ripples formation along the scanning direction.

2. Experiments and theory

2.1. Experimental setup

Experiments on the laser ablation were performed by using the diode pumped nanosecond Nd:YAG laser NL202 (Ekspla Ltd.) with the Gaussian intensity profile. The laser beam was tightly focused

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http://dx.doi.org/10.1016/j.apsusc.2013.03.092

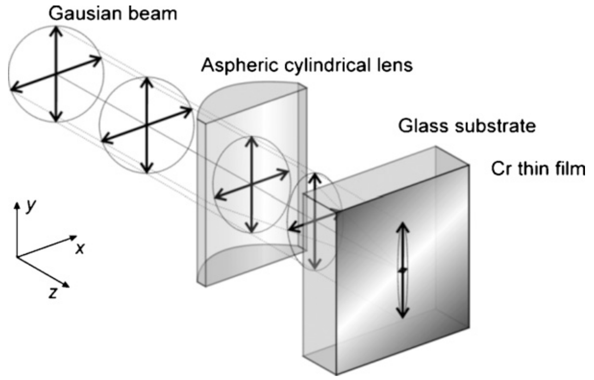

Fig. 1. Principal scheme of the experimental setup. Cartesian coordinate system is denoted by *xyz*.

using the aspheric cylindrical lens the through the glass substrate to chromium thin film (Fig. 1). The shape of the aspheric cylindrical lens was specially designed for optimal focusing to a minimal spot through the glass substrate (the rear-side irradiation). The astigmatic laser spot at the focal position was a high aspect-ratio stripe with the dimensions of $w_{x0} = 2.5\ \mu\text{m}$ by $w_{y0} = 2.5\ \text{mm}$. The spatial energy density distribution in spot is given by:

$$F(x,y) = F_0 e^{-(2x^2/w_{x0}^2)-(2y^2/w_{y0}^2)}, \tag{1}$$

where x and y are the spatial coordinates, $F_0 = 2E_p/\pi w_{x0} w_{y0}$ is the peak laser fluence in the centre of the beam, E_p is the laser pulse energy.

The laser generated radiation with the wavelength of $\lambda = 1064\ \text{nm}$, and the pulse duration FWHM was $\tau_\text{p} = 9\ \text{ns}$. The pulse energy was up to $E_\text{p} = 2\ \text{mJ}$. The laser was operating at the pulse repetition rate of $f_\text{Rep} = 1\ \text{kHz}$ in the regime of the position – synchronized output, controlled by the positioning system (Aerotech Ltd.). The detailed scheme of ripple formation can be found in [9].

The chromium thin film was deposited by vacuum evaporation on a float glass substrate. The thickness of the films h used in experiments was 100 nm. The thickness of the glass substrate was 4.8 mm.

Samples were placed on the high-precision stage ALS25020 (Aerotech Ltd.) and were irradiated with a sequence of partially overlapping laser pulses. The distance between overlapping laser pulses (shift) was precisely controlled by the motion controller and computer. Morphological investigations of the structures were performed by using atomic force microscope (AFM).

2.2. Theory

2.2.1. Plateau–Rayleigh instability

A thin jet of a liquid or a non-moving cylinder of a fluid are unstable to disturbances in radius with period greater than $\Lambda > 2\pi R_0$ and breaks into droplets. This phenomenon is called Plateau–Rayleigh instability [13]. Small perturbations in radius of liquid cylinder grow in time. The capillarity force drives fluid away from the throat, leading liquid cylinder to collapse into droplets. The jet changes in its shape in order to reduce the total surface energy. The fastest growing mode occurs when the period of the disturbance is [13,14]:

$$\Lambda = 9.02 R_0, \tag{2}$$

where R_0 is the radius of the initial un-perturbed cylinder, Λ is the period of the fastest growing mode. The radius of perturbed cylinder grows exponentially in time until it breaks into droplets. The characteristic time scale is given by [15,16]:

$$\tau_0 = 2.74\sqrt{\frac{\rho R_0^3}{\gamma}}, \tag{3}$$

where γ is the surface tension and ρ is the liquid density.

2.2.2. Marangoni convection in liquid metal

Surface tension γ is a thermodynamic property of a liquid which depends on the temperature and other parameters such as chemical composition and surface cleanliness [17]. If the temperature difference is small, the temperature dependence of γ can be linearized in such a way that $\mathrm{d}\gamma/\mathrm{d}T$ is a constant. It has usually a negative value for liquid metals [18]. When the temperature varies substantially along the free surface, the gradient in surface tension $\mathrm{d}\gamma/\mathrm{d}x$ results in a shear force, which causes fluid to move from the hot region to the cold region [19,20]. This phenomenon is called Marangoni effect [21] or capillary convection. The velocity of liquid metal can be calculated using following equation [22]:

$$u = \frac{1}{\eta}\frac{\mathrm{d}\gamma}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x}h, \tag{4}$$

where η is the dynamic viscosity of fluid, h is the thickness of liquid metal and $\mathrm{d}T/\mathrm{d}x$ is the temperature gradient. In thin films irradiated by the Gaussian beam, the Marangoni flow results in formation of dry areas. Surface tension gradient due to the non-uniform heating induces a flow of the molten liquid away from the centre of the irradiated area, leading to formation of dry areas on the substrate [23,24].

2.2.3. Capillarity force

The capillarity force acting on the liquid cylinder which has temperature and radius of curvature gradient is given by [25]:

$$F = 2\pi \int_l \left[\frac{\mathrm{d}r}{\mathrm{d}x}\gamma + r\frac{\mathrm{d}\gamma}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x}\right]\mathrm{d}x, \tag{5}$$

l is the length of the cylinder. The first term in the angle brackets on the right part of the equation is responsible for the capillarity force due to the radius variation along the cylinder. The second term is responsible for thermo capillary (Marangoni) force because of surface tension gradient along the cylinder. This expression shows that the capillary force initiated, for instance, by a small geometrical perturbation has positive increment, tending to drag the liquid material into a larger sphere.

3. Results and discussion

3.1. Experimental self-organization in chromium thin film

The threshold energy density required to remove completely the $h = 100\ \text{nm}$ thick chromium film of the glass substrate with a single laser pulse was estimated as $F_\text{th} = 1.5\ \text{J/cm}^2$ [9]. At this fluence, the central area of the metal film irradiated with an astigmatic laser beam was evaporated (Fig. 2a).

The partially overlapping pulses above ablation threshold formed a complicated structure made of the metal remaining from the ridges (Fig. 2b–c). The resolidified metal structures were made by a series of laser pulses starting from the left side. The beginning of the self-organized chromium on the left was quite irregular (Fig. 2b). The periodical grating was composed at the end of the ripples (Fig. 2c).