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Changes in spectral characteristics of thin molybdenum films with atmospheric annealing

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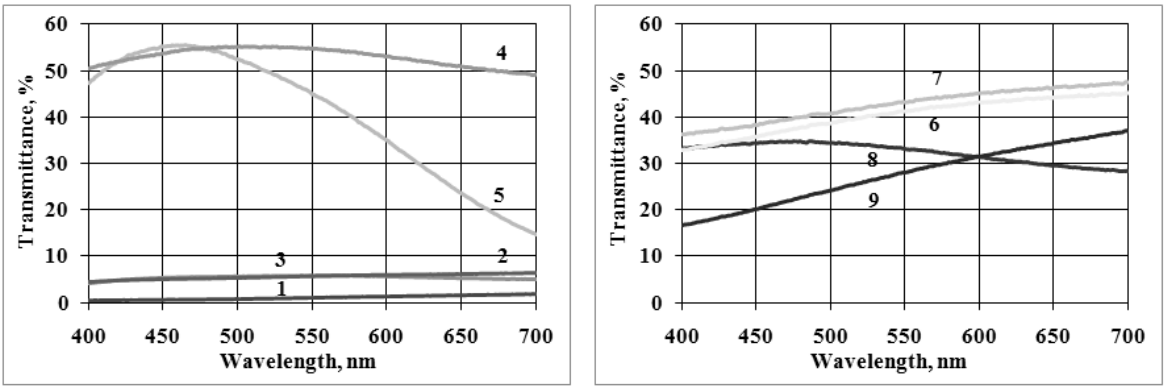
Abstract. In this work the spectral transmission, reflection and absorption of molybdenum films with 35 nanometers thick are investigated. It is established that atmospheric annealing at 600 degrees considerably changes optical characteristics of films. At annealing time of 1 min. the absorption maximum on the wavelength of 532 nanometers is observed. At annealing time more than 1 min. the monotonous increase of scattering caused by increase in a roughness of a sample surface is noted. The studied effects allow to increase resolution of laser record of microstructures.

1. Introduction
Thin molybdenum films are used in the technology of laser thermal chemical writing in producing diffractive optical elements and mask plates [1, 2]. Various physical effects, such as oxidation, melting, evaporation etc. can be observed when a focused laser beam interacts with a molybdenum film [3, 4]. Sub-100 nanometer writing resolution in thick molybdenum films 35-70 nm and improvement of the quality of diffractive elements can be achieved by changing the wavelength, intensity and exposure. A large number of the effects observed make it necessary to investigate physical properties of molybdenum films under different thermal and optical impacts. The aim of the study was to analyze the influence of thermal atmospheric annealing on the optical characteristics of thin molybdenum films.

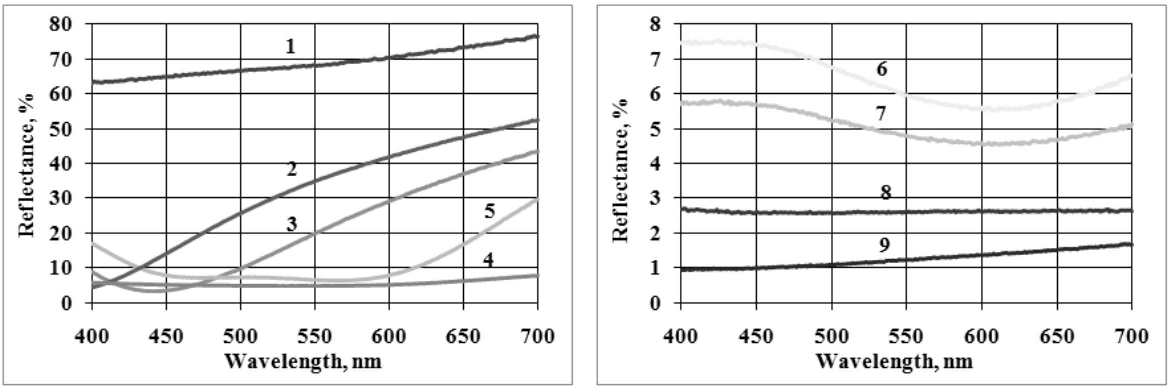
2. Experimental investigation
To carry out the investigation specimens of molybdenum films 35 nm thick were deposited on a silica substrate 2.6 mm thick in vacuum. The surface of the substrate was polished to class 14b according to GOST (State Standard) 2789-59. Spectral transmission of the substrate in the range of 400-700 nm was close to uniform and amounted to 90±1%. After the deposition the molybdenum films were smooth, without visible pinholes or scratches. The films were oxidized at 600ºC during 0-3 minutes with a pitch of 0.25-0.50 minutes in a muffle electrically-heated furnace. Optical absorption of the specimens in the visible range was analyzed on a Shimadzu UV-2450 spectrophotometer. The measurement pitch was 1 nm, the spectral width of the slit- 1 nm with a single scan mode and average scan speed. The device was heated during 2 hours prior to measuring. Measurement noises did not exceed ±0.2% in case of the setting specified.
Transmission T(λ) was measured in the visible range in a convergent beam with the aperture angle of ±5º and ellipticity of polarization 3:1 - 4:1. Fig. 1 shows measured spectral transmission as the function of the annealing time.



a) b)

Figure 1. Film reflection measured for different times of annealing: a) 1-0 min., 2-0.25 min., 3-0.5 min., 4- 0.75 min.,5-1.0 min., b) 6-1.5 min., 7-2.0 min., 8-2.5 min.,9-3.0 min.

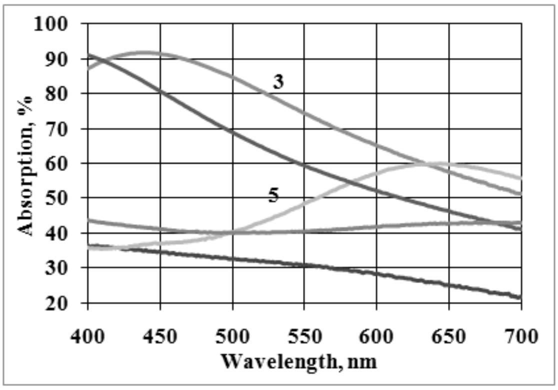
Fig. 2 shows the reflection of specimens R (λ) measured at the striking angle of 5°. The reflection of the film corresponds to the description of its state analyzed by the method of spectral transmission. Scattering of the shortwave part for the specimens with the times of annealing equal to 2.5 min., 3.0 min. (relationships 8, 9 in fig.2, b) is less pronounced due to the influence of aperture properties of the spectrometer reflex attachment used for the analysis of the reflection.



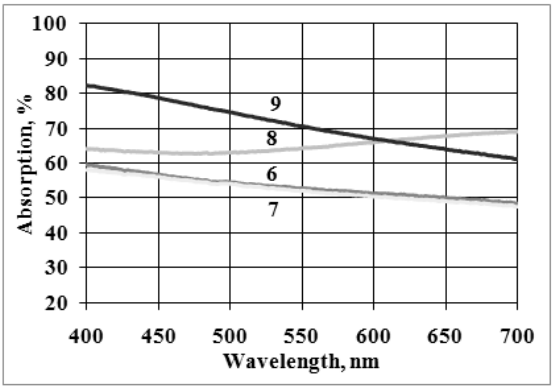
a) b)

Figure 2. Film reflection measured for different times of annealing: a) 1-0 min., 2-0.25 min., 3-0.5 min., 4- 0.75 min.,5-1.0 min., b) 6-1.5 min., 7-2.0 min., 8-2.5 min.,9-3.0 min.

Fig. 3 shows calculated ingestion A (λ) of specimens with the initial molybdenum film thickness of 35 nm. The formula A (λ) =1-R(λ)-T(λ) where R(λ), T(λ) are spectral reflection and transmission, respectively, was used in computations. In case of short time of annealing (0.25-0.75 min.) absorption is increased due to oxidation of the molybdenum film, while in case of a longer period of annealing (0.75-3.0 min.) it happens because the roughness of the oxide film increases in the process of its sublimation at 600 °C.



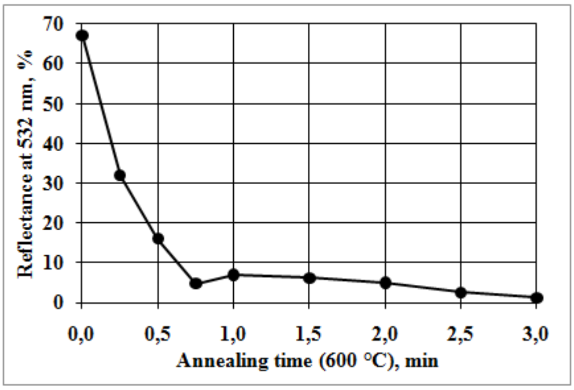
a)



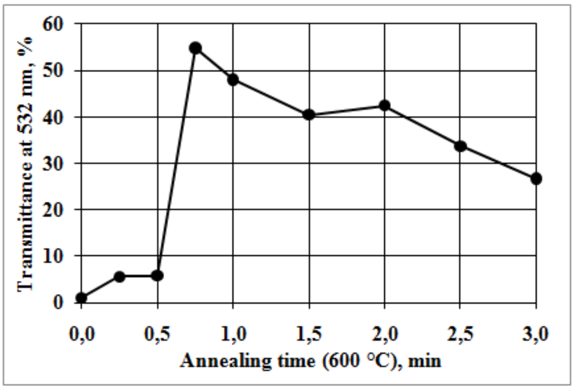
b)

Figure 3. Film absorption computed for different times of annealing: : a) 1 – 0 min., 2 – 0.25 min., 3 – 0.5 min., 4 – 0.75 min., 5 – .1.0 min., b) 6 – 1.5 min., 7 – 2.0 min., 8 – 2.5 min., 9 – 3.0 min.

Figures 4, 5 show changes in transmission, reflection and absorption of the CLWS-200 photomask generator at the wavelength λ=532 nm.



a)



b)

Figure 4. Measured dependence of the film reflection (a) and transmission (b) at λ=532 nm on the time of annealing

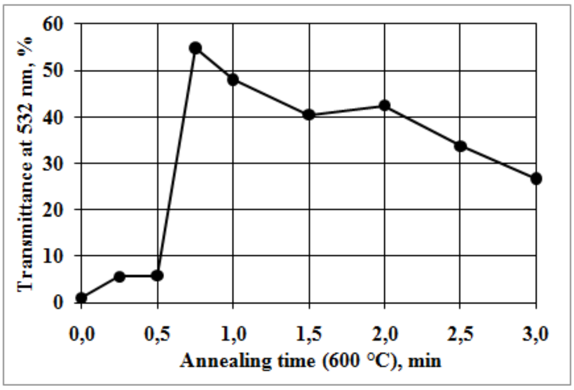


Figure 5. Computed dependence of film absorption at λ=532 nm on the time of annealing

The action of several effects can be seen from fig.4 The first effect is related to the oxidation of the molybdenum film and is accompanied by a sharp decrease of reflection (fig.4, a) and increase of transmission (fig.4,b) of the film in the annealing time range from 0 to 0.75 min. Partial removal of the molybdenum oxide film with the annealing time of 0.50-0.75 min. is also confirmed by the shift of the interference transmission maximum towards short wavelengths (relationships 3,4 in fig.1). The shift corresponds to a decrease of the film design thickness from 140 nm to 110 nm, which also leads to a decrease of absorption (relationships 3, 4 in fig.5 and point 0.50 min. in fig.5).

If the time of annealing exceeds 0.75 min simultaneous decrease in transmission and reflection is observed. This is caused by the scatter of radiation due to increased roughness of the film in its high-temperature sublimation at 600 °C. This is confirmed by the analysis of the annealed film roughness using the Zygo New View 7300 interferometer-profilometer (table 1). As film roughness reduces the transmission and reflection measured the absorption calculated by the expression $A(\lambda)=1-R(\lambda)-T(\lambda)$ increases (fig.5, time 0.75-3.0 min.).

Table 1. RMS of sample profile

Annealing time (min)	RMS (nm)
0	1
0.25	2
0.50	2
0.75	40
1.00	120
1.50	120
2.00	115
2.50	120
3.00	280

3. Conclusion

It follows from the data obtained that the oxidation of a molybdenum film at the initial stage of annealing results in a significant increase of the film's optical absorption, from 32% to 78 % (fig.5). This contributes to increased heat extraction and accelerated ablation of molybdenum-molybdenum oxide films at the centre of the laser Gaussian beam with λ=532 nm, where radiation intensity is the highest. Such coordinate-dependent increase of absorption is equivalent to sharper beam focusing and serves to increase the resolution in case of laser formation of microstructures using the CLWS-200 photomask generator. It should be noted that the absorption measured is typical mostly of molybdenum-molybdenum oxide films. Absorption of silica substrates annealed in the same temperature remained practically unchanged and did not exceed 0.5% in the range of 500 – 600 nm.

Acknowledgments

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References

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