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Study of heat induced changes in elastic properties of multilayer $Mo/ZrSi_2$ membranes

N.I. Chkhalo [a], E.B. Kluenkov [a], A.Ya. Lopatin [a,*], V.I. Luchin [a], N.N. Salashchenko [a], L.A. Sjmaenok [b], N.N. Tsybin [a]

[a] *Institute for Physics of Microstructures RAS, GSP-105, Nizhny Novgorod 603950, Russia*
[b] *PhysTeX, Vaals, Netherlands*

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A B S T R A C T

The paper describes a technique for manufacturing of sub-micron metal membranes based on magnetron deposition of multilayer structures. Tensile stress, biaxial elastic modulus and mechanical strength of 25–50 nm thick multilayer $Mo/ZrSi_2$ membranes were measured, and the behavior of these parameters before and after vacuum heating of samples at the level of heat loads up to 1 W/cm^2 was studied. The elastic properties were obtained from measurements of deformation dependence of the round membranes on the applied pressure differential. A rapid increase in tensile stress of a 25 nm thick $Mo/ZrSi_2$ film was observed at a uniform heat load of 0.25 W/cm^2 which was probably caused by desorption of water molecules from the membrane surface.

1. Introduction

Mechanical stability of thin freestanding films or membranes is an essential requirement for many applications. The constancy of mechanical stresses is the most important condition for the use of membranes as substrates to form patterns with strictly defined geometry. Any changes in the membrane tension during its usage lead to relative displacement of the patterns, which is a serious obstacle to the practical implementation of such schemes as zone-plate-array nanolithography in the extreme ultra violet (EUV) wavelength range [1] or film correction of aberrations of EUV projection lens [2].

Since EUV optical schemes work in a vacuum, one of the main factors impacting the mechanical characteristics of film elements is heating of freestanding films by the absorbed radiation. The only cooling factor of thin films in vacuum is their thermal radiation, so the temperature of films increases significantly even at rather small incident fluxes. Thermal expansion of the material leads to a decrease of the membranes tension or to visual changes of the wrinkles relief (for unstretched films). With an increase in the radiation fluxes and the heating duration, the effects of irreversible changes of the membranes mechanical properties become significant. These effects are caused by the structural changes in the films at a high temperature. Even if the mechanical stability of thin film elements is not a specific requirement for a particular application, these effects have to be taken into account, since the growth of the stress during annealing may cause the rupture of the film.

Currently a lot of studies are being conducted to examine a possibility of using large aperture film elements with an extremely small thickness as pellicles for photomask protection in the tools of EUV lithography. The paper [3] lists the requirements for the EUV pellicle, which is considered to be used in NXE:3300B scanners by ASML. The transparency of the pellicle at $\lambda = 13.5$ nm has to be 90% or higher and the pellicle size is 142×110 mm^2. In practice, such high transparency has not been achieved yet for samples with the required apertures, but the value of 80% has been repeatedly surpassed. The prototypes of the 50–70 nm Si-based pellicles have the transparency of up to 85%. In some former designs thin films of pure Si were attached to supporting meshes [4]; in later designs freestanding polycrystalline silicon membranes were used with thin capping layers of silicon nitride or Ru [5]. The full-size membranes made of pure Si_3N_4 with a thickness of 16–20 nm and the transparency of 89.5% were also demonstrated [6], as well as thicker films of the same material (about 30 nm) with an array of etched dimples [7], enabling to reach the pellicle transparency of about 85%.

A drawback of silicon and silicon nitride is weak absorption in the visible and near IR spectral range resulting in low emissivity of membranes (<1–2%) and, consequently, in the elevated temperatures under quite moderate loads. An example of membrane destruction after a short heat load of 0.4 W/cm^2 is described in [8]. Graphite [9] and metal films featuring much higher emissivity demonstrate better thermal stability.

The prototypes of membranes for the pellicles on the base of multilayer metal films with the transparency of 86% at $\lambda = 13.5$ nm were fabricated with a diameter of up to 80 mm [3]. Comparative tests of heat

* Corresponding author.
E-mail address: lopatin@ipm.sci-nnov.ru (A.Y. Lopatin).

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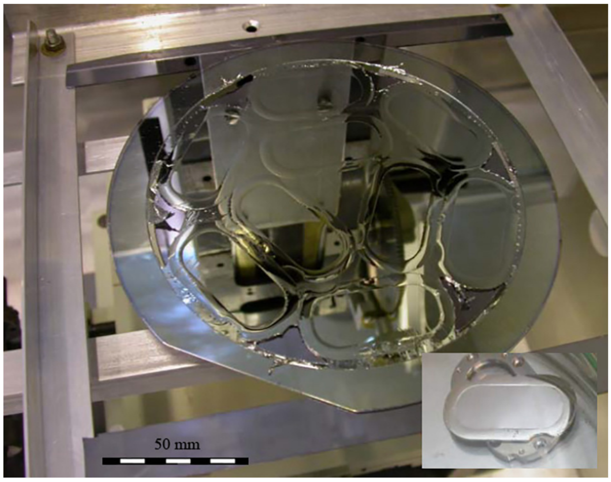

Fig. 1. Group fabrication of multilayer Mo/$ZrSi_2$ membranes 37 × 16 mm. Film thickness is about 50 nm. The initial stage of separation to individual membranes is shown in the main photograph, one of the ready samples (after the removal of polystyrene) – in the tab.

load withstandability were fulfilled for a number of freestanding multilayers with a high transparency at 13.5 nm [10,11]. The composition Mo/$ZrSi_2$ with $MoSi_2$ coatings has been found to be the most promising among the tested films. This composition was discovered to withstand vacuum heating at an absorbed power density of 4–5 W/cm^2 almost without degradation of optical properties and without mechanical damage in the heated area during multi-hour exposures.

This paper describes the procedure for fabrication of multilayer metal films as stretched membranes and the technique for measurements of the membrane tension, elastic modulus and mechanical strength. The elastic characteristics and their changes under temperate heat loads are determined for the 25–50 nm thick Mo/$ZrSi_2$ membranes.

2. Experimental details

2.1. Fabrication of thin film metal membranes

Our basic approach to fabrication of freestanding multilayer films was discussed in details in [11]. Though it was originally applied to create Zr or Mo based film filters with a high transparency near $\lambda =$ 13.5 nm, it allows also fabricating films of many other materials. In particular, Al/Si mesh supported multilayers were designed for solar astronomy [12] and then were successfully used in space missions TESIS [13] and Hi-C [14].

If film samples are needed in the form of stretched membranes, the general technique of fabrication [11] becomes complicated. First of all, multilayer films, which are <50 nm in thickness, are strengthened by an additional polymeric layer. The layer of polystyrene of about 100 nm in thickness is spin coated onto the substrate with a sputtered structure. This layer is deleted by UV radiation after the completion of all the rest technological operations on the film sample fabrication. In order to stretch the freestanding film, the fished up and dried film on a frame is moistened by glue along its boundary and then is heated on a hot plate with a temperature of 110–130 °C. Fast drying and shrinkage of the glue take place during the heating. Wrinkles which chaotically cover the film surface are dragged to the edge and fixed there as the glue hardens. The expected result of the stretching procedure is a wrinkle-free mirror-like film surface with uniform tension in its plane.

When membranes of small apertures are produced, we commonly use the group technique for their fabrication. It consists in concurrent gluing of several frames to the stretched film of a large aperture. The frames are spread with the glue and are placed onto an adjustable plate; the frame with the stretched film is lowered smoothly until the film comes into contact with the glued surfaces. The procedure is illustrated in Fig. 1: nine oval frames with inner sizes of 37 × 16 mm are glued to a 50 nm thick multilayer film which is stretched over a diameter of 123 mm; one of completed framed membranes after the separation and removing of polystyrene is shown in the tab. Besides the reduction of the fabrication time, the group technique gives a number of advantages. Less uniform in stretching peripheral area of the film may be eliminated. Very reliable fixation of the film edge is achieved with the usage of the epoxy glue.

2.2. Technique for study of mechanical properties and their behavior during heating

The biaxial elastic modulus and initial tension of round membranes were determined from the comparison of the theoretical and experimental dependencies of deflection w on applied pressure q. For the study of changes in the mechanical properties under heat loads, the membranes were heated in a vacuum by the laser radiation with a wavelength of 808 nm. The laser power was sufficient to heat the samples 25 mm in diameter with the absorbed power density of up to 0.25 W/cm^2 over the whole surface or even with higher intensity – in the local area of the samples. The intensity of heating up to 1 W/cm^2 of the absorbed power density and the duration of up to tens of hours were used in this work. The heat load was calculated as the measured value of the incident power density multiplied by the film absorptivity obtained from optical measurements. In all exposures the laser beam was modulated by a shutter in the proportion 1.5 s 'on'/0.1 s 'off'. The film temperature was monitored online by a pyrometer. The value of emissivity 20% was taken for each of the tested Mo/$ZrSi_2$ membranes since it was measured [11] for a 50 nm thick structure containing 2.5 nm of Mo and 1.5 nm of $ZrSi_2$ in a bilayer.

The influence of long-term heat loads on the rupture strength of the samples and the change in the initial tension in membranes during short heating cycles were both investigated. In the latter case we used to interrupt the heating in order to measure dependence $w(q)$. The membrane was removed from the chamber and in-air measurements of the membrane deflection under a pressure differential were made

Table 1
Summary characteristics of studied membranes.

Composition of multilayer films	T, %		Test conditions		Y, GPa
	$\lambda = 13.5$ nm	$\lambda = 633$ nm	P, W/cm^2	τ, h	
Ru-2,($ZrSi_2$-1.5,Mo-2.5)*10, $ZrSi_2$-1.5,Ru-2	72.3	0.75	1	15	340
$MoSi_2$-3,(Mo-2.5,$ZrSi_2$-1.5)*11, Mo-2.5,$MoSi_2$-3	72.5	1.0	0.4	40	–
$MoSi_2$-2.5,(Si-7,$ZrSi_2$-1)*4, Si-7,$MoSi_2$-2.5	86.5	11	–	–	–
Ru-2,(Mo-1,$ZrSi_2$-1.5)*7, Mo-1,Ru-2	81.0	4.8	0.25	0.08	435

T - measured transparency of samples before heating, P - the density of absorbed power during heating tests, τ - the duration of heating, Y - measured biaxial elastic modulus of unheated films.