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Mo/Si-multilayers for EUV applications prepared by Pulsed Laser Deposition (PLD)

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Abstract

In the past, the successful application of PLD for X-ray multilayer synthesis has already been demonstrated for C-spacer systems. Recently, the method has also been tested for Mo/Si layer stacks. A UHV-coating machine has been used to prepare X-ray mirrors on 4 in. substrates. The ablation of both Mo and Si targets was carried out by Nd:YAG laser irradiation using the third harmonic ($\lambda = 355$ nm) with a pulse energy $E_p = 275$ mJ and a pulse width $\tau = 4 \ldots 6$ ns. Multilayers of 10 . . . 50 periods have been synthesized. Soft X-ray measurements in the EUV-range at near normal incidence show reflectivities R_s of typically 60%. From HRTEM, a high stack regularity and minimum interface roughness can be deduced. In contrast to conventional technologies (coating by sputtering or e-beam evaporation) the formation of a $MoSi_x$-interface layer happens only when depositing Mo on Si. Extremely sharp interface transitions from one individual layer to the other are observed and the total period is represented by a three-layer system. From TEM results, a structure model for PLD-prepared Mo/Si-multilayers has been deduced. The optical parameters of the layers were adapted by reflectivity curve fitting, so that the results measured in the EUV-range can be explained. Using this model, predictions of the ratio of the number of atoms N_{Si}/N_{Mo} for the total stack were made and are in good agreement with results of RBS measurements. The use of the multilayers as X-ray optics requires an excellent homogeneity of the layer thickness across the entire mirror. It can be shown that the PLD technique is able to realize film uniformities with a standard deviation of the period thickness of less than 0.5%. This was confirmed by Cu–Kα-reflectometry and by near normal incidence measurements in the EUV range on 4 in. samples.

1. Introduction

In the past, the successful application of the PLD process for X-ray multilayer synthesis has already been demonstrated for C-spacer systems. Particularly Ni/C multilayers with graded period thickness on curved substrates were successfully used as Goebel-mirrors in commercially available X-ray reflectometers and diffractometers. The aim of the present paper was to investigate the potential of the PLD for the preparation of high-reflectivity Mo/Si multilayers for the Extreme Ultraviolet Lithography (EUVL).

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According to the literature, nearly all Mo/Si multilayers have been prepared by the deposition methods e-beam evaporation, magnetron sputtering and ion beam sputtering. To our knowledge, only three publications concerning the synthesis of Mo/Si multilayer stacks by PLD exist. Kim et al. [1] used the second harmonic of a Nd:YAG pulsed laser ($\lambda = 532$ nm, pulse duration $\tau = 5$ ns) and measured a near normal incidence reflectivity of 1.2% at 15.6 nm. The low reflectivity was attributed to the vacuum environment (10^{-3} mbar) which caused a significant carbon and oxygen contamination of the multilayer. Weaver et al. [2] performed the ablation of the target material by a KrF excimer laser ($\lambda = 248$ nm, $\tau = 23$ ns) at a base pressure of $5 \cdot 10^{-9}$ mbar. The normal incidence reflectivity of a multilayer with 11 periods was determined using a lead laser–plasma soft X-ray source and has a value of 7.3% at 19.0 nm. The reflectivity loss compared to theoretical predictions was attributed to the properties of surface and interface boundaries within the structure and to non-abrupt transitions from one material to the next. Dietsch et al. [3] reported about the interface formation in Mo/Si multilayers in dependence on the laser wavelength λ_{laser}. From HRTEM investigations, it was concluded that with decreasing λ_{laser}, sharper transitions between the individual layers occur. Starting from this point, we continued our work on the Mo/Si system and evaluated the potential of the PLD as an industrially applicable method for coating optical components for the EUVL.

2. Multilayer preparation

The large area Pulsed Laser Deposition method [4] enables the deposition of thin films of high reproducibility. A scheme of the PLD principle is shown in Fig. 1: A rotating target holder contains up to four interchangeable targets. The laserbeam–target interaction leads to the emission of target material, the so-called plasma plume, in a state far from the thermodynamical equilibrium. This material is deposited onto the substrate in a distance of about 150 mm. To increase the target life-time and to improve the layer homogeneity, the target is moved in two directions. The substrate motion and a shaped slit between target and substrate ensure the layer thickness homogeneity over the entire 4 in. substrate.

The ablation was carried out by Nd:YAG laser irradiation using the third harmonic ($\lambda = 355$ nm) of the basic wavelength ($\lambda = 1064$ nm) in a vacuum chamber at a base pressure of $1.0 \cdot 10^{-8}$ mbar and a working pressure of $< 5.0 \cdot 10^{-8}$ mbar. The pulse energy E_p was 275 mJ, the pulse duration $\tau = 4 \ldots 6$ ns.

3. Cu–Kα reflectometry

For X-ray reflectometry with Cu– and Mo–Kα radiation, the Twin-Göbel mirror (TGM) arrangement is used [5]. The following parameters are typical values:

- Primary beam intensity $I_0 > 1.0 \cdot 10^{+9}$ cps (Cu $K\alpha_1 + K\alpha_2$)
- Suppression of Cu–Kβ radiation at a ratio of 1 000 000:1
- Beam divergence $< 0.02°$

From small angle X-ray reflection, substantial information about the multilayer structure can be

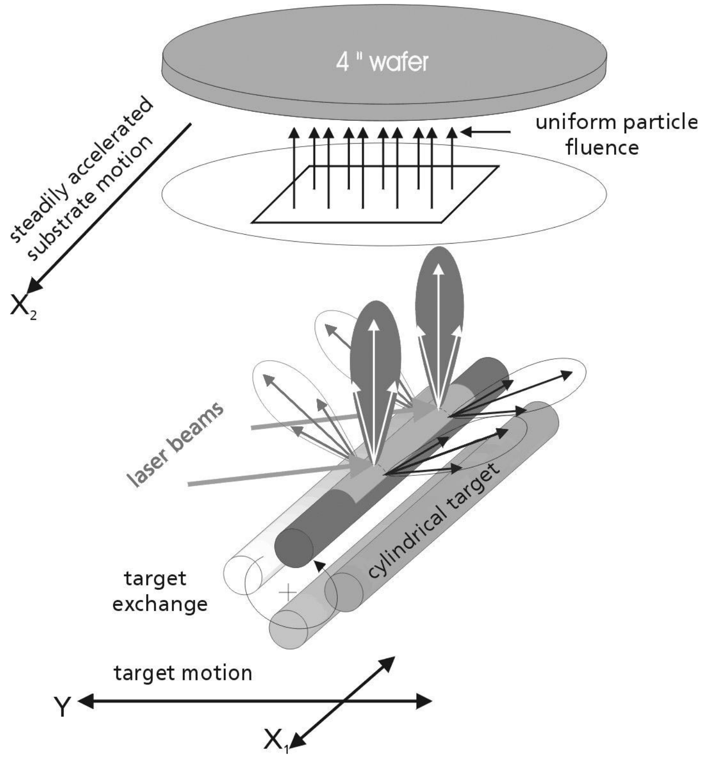

Fig. 1. Principle of thin film deposition by Pulsed Laser Deposition [4].

derived: regularity of the stack, period thickness d_{period}, layer thickness ratio $\Gamma = d_{\mathrm{Mo}}/d_{\mathrm{period}}$, interface roughness and diffusion σ.

The stability of the coating process is essential to achieve optics of high reflectivity and to ensure the run-to-run reproducibility, which is necessary to prepare multilayers with specific thickness profiles. In the Cu– and Mo–Kα reflectographs, the full width of half maximum of the Bragg peaks is a very sensitive measure of the regularity of a multilayer stack and gives information about the stability of the coating process. In Fig. 2, the Cu–Kα reflectograph of a typical Mo/Si-multilayer is shown and indicates that no significant broadening of the higher order Bragg peaks is observable. Thus, with PLD, the regularity of the stack can be guaranteed. Furthermore, the number of detectable Bragg peaks denotes that the interface roughness must be very low. A real value will be given in Section 5 where a layer model is developed which takes into account all results of the performed characterization methods.

4. HRTEM investigations

In addition to reflectometry cross-section transmission high-resolution electron micrographs (HRTEM) provide information about the geometrical structure, the interface roughness and diffuseness. Specimen micro-cleavage and very careful TEM observation reveal a layer structure which is

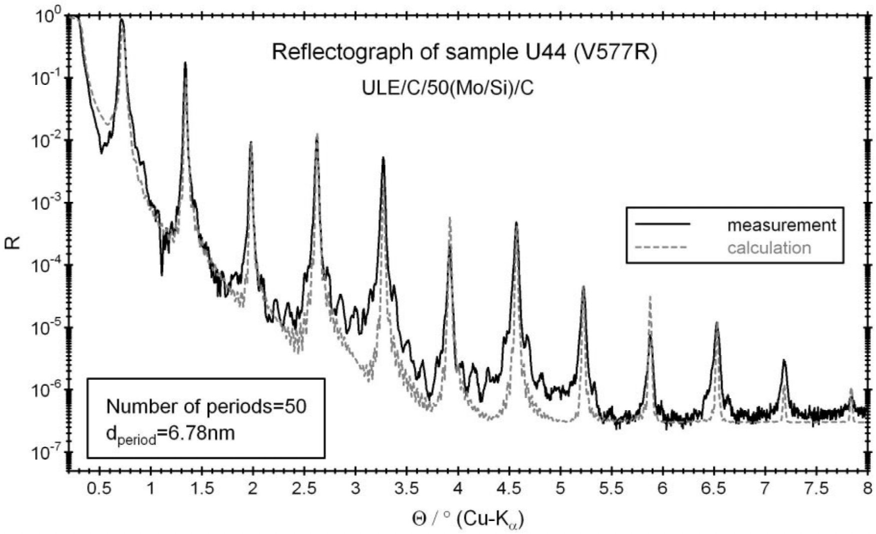

Fig. 2. Cu–Kα reflectograph of a typical PLD-prepared Mo/Si multilayer. The calculated reflectograph was performed using the multilayer parameters from Section 5.

different in comparison to layer structures of magnetron sputter deposited multilayers (Figs. 3 and 4). The following conclusions from HRTEM investigations can be stated:

- extremely smooth interfaces between the different layers
- different interfaces Mo on Si and Si on Mo, for Mo on Si formation of transition layers with sharp interfaces to adjacent layers

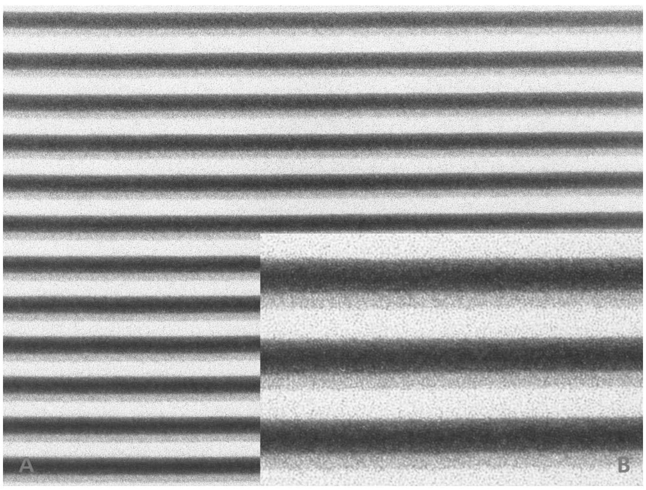

Fig. 3. (A) HRTEM cross-section of a PLD-prepared Mo/Si multilayer. The coating direction is from bottom to top. (B) Magnified representation of three periods of the stack showing atomically flat interfaces.

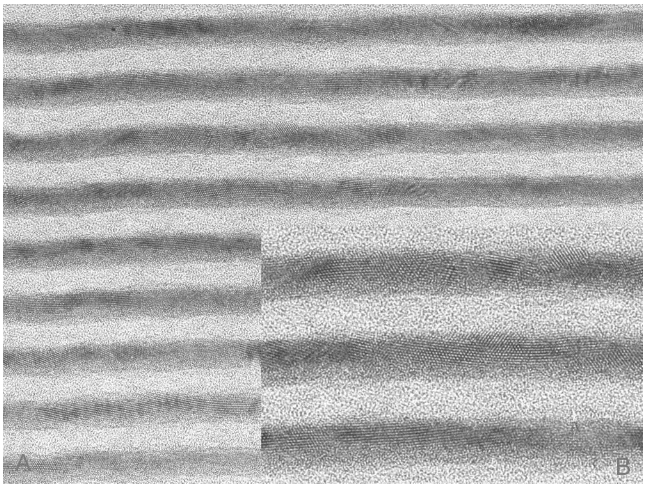

Fig. 4. (A) HRTEM cross-section of a magnetron sputtered Mo/Si multilayer. (B) Magnified representation: (i) two transition layers with different thickness and increased roughness compared to the PLD-multilayer; (ii) polycrystalline Mo layers.

- in contrast to magnetron sputtered Mo/Si multilayers (Fig. 4) having polycrystalline Mo-layers no lattice fringes are found, all individual layers are amorphous

5. Multilayer model and EUV-reflectivity

Because of the high number of free parameters, the adaptation of calculated reflectographs to measured is a very time-consuming task and practically impossible to fit a measured reflectograph in every detail.

From Cu–Kα reflectometry, the period thickness d_{period} and the mean density of the stack can be calculated exactly. All other parameters can only be determined by fitting procedures. Therefore, it is helpful to have supplemental investigations like HRTEM and RBS to confirm the layer model.

As a result of HRTEM investigations for PLD prepared Mo/Si multilayers, a layer stack model with three individual layers per period can be developed. The thicknesses of the layers are: $d_{absorber} = 0.420 \cdot d_{period}$, $d_{transition} = 0.196 \cdot d_{period}$, $d_{spacer} = 0.383 \cdot d_{period}$. With $d_{period} = 6.78$ nm, obtained by Cu–Kα reflectometry, the geometrical data of the layer stack are known. The optical parameters still must be determined. This can be done by adapting the calculated Cu–Kα and EUV reflectographs to the measured curve. As a supposition, we defined that the transition layer consists of amorphous $MoSi_2$. There was no possibility to prove this assumption, but keeping in mind that $MoSi_2$ is a rather stable chemical compound, it should be reasonable that the short-range order of the transition layer is similar to that found in crystalline $MoSi_2$.

Using the IMD-software [6], the following layer model was determined:

a–C: $d = 0.30$ nm, $\sigma = 0.15$ nm (err. fun.)
$Si_{0.93}Mo_{0.07}/MoSi_2/Mo_{0.70}Si_{0.30}$ multilayer, $N = 50$, $d = 6.78$ nm:

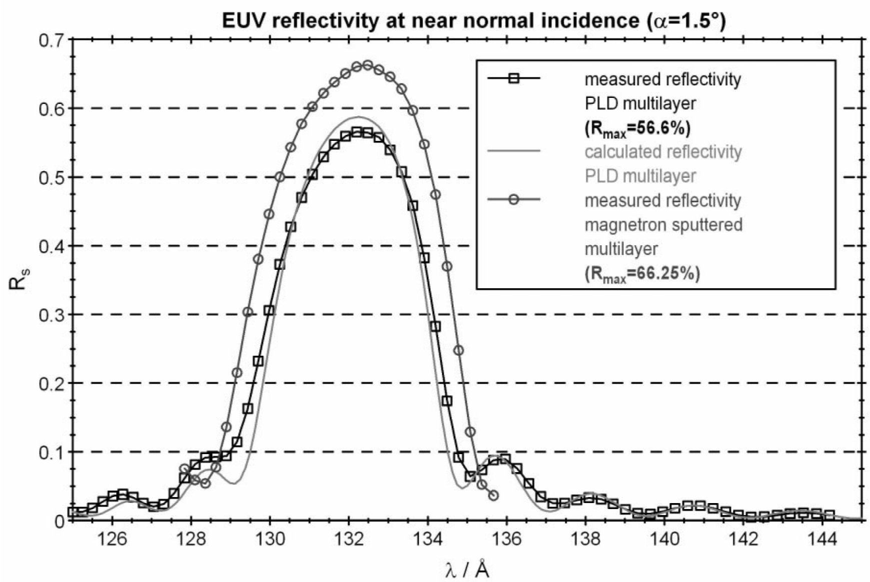

Fig. 5. Calculated and measured EUV reflectivities of a PLD-prepared Mo/Si multilayer. Due to droplets, a loss of reflectivity of about 3% occurs. This was taken into account by fitting the measured curve. For comparison, our results obtained with magnetron sputtered Mo/Si multilayers are also shown.

$Si_{0.93}Mo_{0.07}$: $\rho = 2.4$ g/cm^3, $d = 2.60$ nm, σ(a–C/$Si_{0.93}Mo_{0.07}$) = 0.20 nm (err. fun.), σ($Mo_{0.70}Si_{0.30}$/$Si_{0.93}Mo_{0.07}$) = 0.20 nm (err. fun.)
$MoSi_2$: $\rho = 5.3$ g/cm^3, $d = 1.33$ nm, $\sigma = 0.63$ nm (err. fun.)
$Mo_{0.70}Si_{0.30}$: $\rho = 8.1$ g/cm^3, $d = 2.85$ nm, $\sigma = 0.20$ nm (err. fun.)
a–C: $d = 2.5$ nm, $\sigma = 0.25$ nm (err. fun.)
a–SiO_2: $d = 2.0$ nm, $\sigma = 0.43$ nm (err. fun.)
Si substrate: $\sigma = 0.15$ nm (err. fun.)

The agreement of the calculated and measured reflectographs is shown in Fig. 2 (Cu–Kα) and Fig. 5 (EUV). Due to droplets on the surface of the PLD prepared multilayers, only 95% of the coated substrate area contributes to the reflection. Without droplets, the reflectivity would be about 3% higher. This was taken into account by fitting the EUV reflectivity.

6. Coating uniformity

In the beginning of preparing coatings by PLD, a very critical point was the strong inhomogeneity of the film thickness. This was caused by the plume characteristics with its strong spatial dependence of the particle flux. With the target-substrate arrangement developed by the FhIWS Dresden (Fig. 1), it became possible to coat homogenous layers on 4 in.-substrates. For the Mo/Si multilayers, the following standard deviations were measured:

- period thickness: $\sigma < 0.5\%$
- EUV peak reflectivity: $\sigma < 0.4\%$

These values are remarkable results for thin films prepared by PLD. Very recently, we succeeded to further improve the uniformity using the magnetron sputter deposition technique and determined the following findings at 4 in. substrates:

- period thickness: $\sigma \leq 0.033\%$
- EUV peak reflectivity:
  - $\sigma = 0.08\%$ at fixed near normal incidence angle $\alpha = 1.5°$ ($R_{max} = 68.49\%$)
  - $\sigma = 0.186\%$ at fixed photon energy $E = 99$ eV ($\lambda = 12.52$ nm) ($R_{max} = 67.97\%$)

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