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Optical properties and oxidation resistance of different transition metals for soft X-ray and EUV applications

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ABSTRACT

The results of a comparative study of Ru-, Mo-, Nb- and Pd- coatings designed for grazing angle applications in the soft X-ray and extreme ultraviolet (EUV) spectrum are presented. Optical properties and temporal stability of coatings were investigated using EUV reflectometry at 13.5 nm and grazing incidence X-ray reflectometry (GIXR) with Cu-Kα radiation. Nb- and Mo-coatings showed a strong inclination to surface oxidation at ambient atmosphere leading to reflectivity losses. The Pd coating as a noble transition metal showed the highest oxidation resistance over a period of one year. The best reflective properties at 13.5 nm were achieved by Ru coatings. GIXR simulation results of the time dependent surface oxidation were used to predict the reflective properties of the studied coatings following four months of storage in an ambient atmosphere for a wide spectral range (5.0 nm–40.0 nm).

1. Introduction

In the soft X-ray and extreme ultra violet (EUV) spectral regions, grazing incidence mirrors have a wide range of applications. Solar imaging spectrometers observe the hottest parts of the corona such as flares and active regions (0.1 nm–100 nm) with grazing incidence mirrors [1]. Such spectrometers are implemented on board space mission SOHO [2] and others such as TRACE [3] or SDO [4].

A further application is the EUV lithography (EUVL), which is planned for patterning features <8 nm [5] using a wavelength of 13.5 nm. Grazing incidence collector optics are commonly used to collect radiation from the EUV source in a wide angular range [6,7].

The degradation of grazing incidence mirrors caused by surface contamination and surface oxidation of the optical coatings under real environmental conditions is a current research topic because it leads to considerable reflectivity losses. Hence, it is important to understand the degradation kinetics and the main degradation mechanisms which are responsible for reflectivity losses of mirrors. It has previously been shown by different groups that ion debris buildup or erosion [8–10], carbon growth [11–13] and surface oxidation [14] result in a reduction of the reflective properties. Regarding stable and high-reflective optical performance, state of the art coatings are made from Au [1,15,16] Pt [17], Pd [16] and Ir [18] for grazing incidence spectrometers and from Ru [7,19], Au [20] and Pd [20,21] for EUVL collector optics. High-density transition metals have high theoretical reflection properties at 13.5 nm [7]. Chkhalo et al. reported on grazing incidence mirrors in the wavelength range of 0.8 nm–18 nm and introduced a new bilayer design to enhance the reflective properties based on high-density and low-density materials [22]. Simulated reflective properties of Au, Ni, W, Al, Ni, Os, Rh, C, Cr were presented. In our paper some new elements (Ru, Mo, Nb, Pd) were investigated in terms of the temporal stability and reflection properties in the soft X-ray and EUV spectral regions. Due to cost issues and radioactivity respectively, rhodium (Rh) and technetium (Tc) were not considered.

2. Experimental

Mirror coatings were fabricated on the DC-magnetron sputtering system MRC-903 [23]. In this industrial system, coatings were deposited in pure Ar atmosphere with a working pressure of 1 mTorr and a source power of 500 W. The background pressure was $5 \cdot 10^{-7}$ Torr and all targets had a purity of 99.9%. Super-polished silicon wafers with crystal orientation of ⟨111⟩ were used as substrates. These wafers have a surface roughness of approximately 0.15 nm.

All produced samples were measured by grazing incidence X-ray reflectometry (GIXR) with Cu-Kα radiation ($\lambda = 0.154$ nm) to characterize the coating properties. The GIXR data are fitted with a two-layer model (transition metal + metal oxide) using the Leptos 7 software

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package from Bruker [24]. In order to compare materials with different surface chemical reaction properties, the ideal stoichiometric metal oxides with the lowest enthalpies of formation (ΔH) were selected for simulations as a model that is as simple as possible (RuO_2: −305.0 kJ/mol; MoO_3: −745.1 kJ/mol; Nb_2O_5: −1899.5 kJ/mol; PdO_2: −85.4 kJ/mol) [25]. The difference in enthalpy of formation between reaction products and educts describes the required energy for a phase transformation. Therefore, the enthalpy of formation was chosen as a parameter to find the most stable oxides, thus the expected final state. The extracted simulation results provide information on the coating thickness, coating density and surface roughness.

The EUV reflectometry (EUVR) was carried out by the *Physikalisch Technische Bundesanstalt* (PTB) [26] at a fixed wavelength of 13.5 nm in the grazing angle range up to 30° using s-polarized radiation. The experimental setup at the PTB and size of the samples permitted a minimum grazing angle of 2.5°. All EUV reflectivities were measured approximately two weeks after deposition with the exception of the Pd coating which was measured 253 days after deposition. The reflectivity curves were simulated with the software *Film Wizard* developed by SCI [27]. The optical constants of the materials were calculated from the cxro-database [28]. This database is based on the optical constants of Henke et al. [29] and was updated for some materials often used in the soft X-ray and EUV spectral range, e. g. Ru and Mo. Similar to GIXR simulations, a two-layer model (transition metal + metal oxide) with ideal interfaces (without roughness and intermixing) was used as a first approach here. The simulated reflection curve is brought into compliance with the experimental data by fitting the layer thicknesses with a simplex algorithm (implemented in *Film Wizard*).

3. Results and discussion

3.1. Coating properties

The soft X-ray and EUV optical performance and, in particular, the critical angle of the total external reflection correlates with the density of the deposited coating [30]. If the density is increased, the critical angle will rise, too. Therefore, a high-density coating with low absorption will be the best choice for high reflective coatings operating at grazing angles. Immediately after deposition, Ru-, Mo-, Nb- and Pd- coatings were characterized using GIXR. All results regarding coating thickness, coating density and surface roughness are given in Table 1.

According to the GIXR results, the densities of the as-deposited Ru-, Mo- and Pd- coatings are similar to the bulk densities (Table 1). The Nb coating exhibits the lowest density of 8.4 g/cm^3, which is slightly lower than the Nb bulk density (8.6 g/cm^3). All deposited coatings have thicknesses of approximately 35 nm and show surface roughness below 1 nm RMS. An additional layer was found on top of the Ru-, Mo- and Nb- coatings. With GIXR measurements it is not possible to identify the chemical composition of coatings, because this method is only sensitive to the electron density contrast between thin films. Due to the simulated density of the surface layer that fits to the particular metal oxide, it was associated with an ideal stoichiometric surface oxide. Based on the two-layer simulation model, the oxide thicknesses were determined and are presented in Table 1. It should be noted that the as-deposited Pd coating does not show any surface oxidation, so a single layer model was used for simulation.

3.2. Optical properties

The measured reflectivity data of the coatings were integrated in the grazing angle range from 2.5° to 20° and were called integral reflectivity R_{meas}. R_{meas} normalized with the one calculated for a non-oxidized thin film (ideal, theoretical integral reflectivity R_{theo}) was used to characterize the optical properties of the studied coatings. The second parameter used to estimate the optical performance is the critical angle of the total external reflection (Θ_{crit}) which is conventionally defined as the angle where the reflection decreases to 50% (Table 2). Theoretical and experimental reflectivities measured at the wavelength of 13.5 nm on grazing angles are shown in Fig. 1.

The Ru coating showed the highest integral reflectivity R_{meas} of 14.6 of all deposited coatings (Mo: 14.1; Pd: 13.5; Nb: 12.7). Considering the parameter R_{meas}/R_{theo}, the best optical performance was achieved by the Pd coating. It was found that the measured reflectivity of the Pd coating was higher than in theory ($R_{meas}/R_{theo} = 1.03$). This contradiction can be explained by the mismatching optical constants of the deposited Pd coating and the calculated Pd layer. All other deposited coatings showed reduced reflectances R_{meas} compared to those calculated (Table 2). Mo- and Nb- coatings had a maximum gap between the measured and calculated reflectivities (Mo: $R_{meas}/R_{theo} = 0.90$; Nb: $R_{meas}/R_{theo} = 0.82$). These reflectivity losses could be explained by surface degradation due to surface oxidation as it was simulated in Fig. 2. It is known that the edge of total external reflection at Θ_{crit} becomes smoother because of strong absorption [30]. The distinctive deviation of the measured curve shape from that calculated confirms the assumption of surface oxidation. Further EUVR-simulations showed that reflection losses due to rough surfaces would lead to a homogenous decrease in reflection across the entire angle range without changing the curve shape (not shown in this paper). A superposition of surface oxidation and carbon contamination as degradation processes cannot be eliminated without chemical analysis but is neglected here in order to compare different materials with a model that is as simple as possible.

Furthermore, the Ru coating had the highest critical angle of $\Theta_{crit} = 25.0°$ (Table 2). The critical angles of Mo- and Nb- coatings were smaller than that of Ru with 21.2° and 18.2°, respectively. Based on the GIXR results, this was expected due to a decreased density of the coating material (Table 1). The critical angle of the Pd coating was 22.6° and lower compared to the Ru, even though the density of the Pd coating was nearly the same as the Ru coating (Table 1). The Pd coating also showed a curve shape without the characteristic plateau for total external reflection although no surface oxide was found for this material. This can be explained by a higher absorption of Pd coating at 13.5 nm compared with the Ru coatings [29].

3.3. Oxidation resistance

Surface oxidation of grazing incidence coatings is a crucial factor for the degradation of reflectivity [14]. As a consequence of surface oxidation, the reflectivity will decrease due to the high absorption of oxygen in the EUV region as shown in Fig. 2. On the example of Ru, several theoretical simulations were carried out to compare surface oxidation with other possible degradation mechanisms such as carbon growth and development of surface roughness. These simulations showed that formation of a surface oxide with a thickness 2 nm on top of a 40 nm Ru

Table 1
Theoretical and measured properties (GIXR) of as-deposited coatings.

Coating	Ruthenium (Ru)	Molybdenum (Mo)	Niobium (Nb)	Palladium (Pd)
Bulk density [g/cm^3] [31]	12.45	10.28	8.57	12.02
Coating density [g/cm^3]	12.5 ± 0.1	10.3 ± 0.1	8.4 ± 0.1	12.0 ± 0.1
Coating thickness [nm]	40.5 ± 0.2	35.4 ± 0.2	29.1 ± 0.2	30.4 ± 0.2
Oxide thickness [nm]	0.7 ± 0.2	1.1 ± 0.2	1.3 ± 0.2	–
Surface roughness [nm]	0.9 ± 0.1	0.9 ± 0.1	0.6 ± 0.1	0.8 ± 0.1