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X-ray gratings and projection lithography by means of laterally structured multilayers

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Abstract. — Starting from multilayer systems as X-ray mirrors with a high normal incidence reflectivity (for example measured to be 60% at 14 nm), laterally structured multilayers serve as X-ray optical components such as gratings and reflection type masks for X-ray lithography. Mo/Si (30 bilayers) and Mo-Si/Si multilayer systems (33 bilayers) are fabricated by electron beam evaporation in UHV. Analysis of the quality of the stack is made by using an in situ monitoring system measuring the reflection of the C-K line (4.47 nm) and ex situ grazing incidence X-ray reflection of the Cu-Kα line (0.154 nm). A smoothing of the boundaries is obtained by thermal treatment of the multilayer system during growth and by ion polishing. The microstructure of the multilayer systems is investigated by means of Rutherford Backscattering, Sputter/AES techniques, electron-microscopy, scanning tunnel microscopy and atomic force microscopy. Baking the final stack after deposition up to 900 °C is applied to study its thermal stability. This paper reports the figure of merits of laterally structured multilayers such as X-ray gratings when laterally structured silicon wafers are coated with multilayers, or masks for X-ray projection lithography when multilayer mirrors are structured by reactive ion etching.

1. Mo/Si multilayers as X-ray mirrors and their thermal stability.

Multilayer systems of alternating high and low absorbing material are able to serve as X-ray mirrors on the basis of constructive interference of reflected partial waves [1]. In the wavelength region between 13 nm and 30 nm the combination of Mo and Si is most widely used for normal incidence multilayer mirrors. High reflectivities have been achieved with sputtering as the preparation technique [2, 3]. The present paper reviews data of multilayer systems produced by e⁻-beam evaporation in UHV, where during the deposition the reflectivity of the stack is measured in situ by means of soft X-ray C-K radiation [4]. It has been found that in the competition between lateral mobility and interface roughness on the one hand and vertical diffusion and smearing out the boundaries of the interfaces on the other hand, there is an optimum deposition temperature of the multilayer stack at between 150 °C and 175°C depending upon the deposition rates, achieving best normal-incidence reflectivities [5].

Figure 1 shows the typical experimental result of the normal incidence reflectivity obtained for a multilayer system consisting of 30 pairs of Mo/Si deposited at the optimized substrate
temperature of 150 °C on a Si wafer (dashed curve [6]). A small micro-roughness obtained, which does not increase in the layer stack and is given by the substrate roughness measured as being 0.5 nm means of Cu-K$_\alpha$ X-ray diffraction, TEM and STM, was the most important precondition to get normal incidence reflectivities of up to 60 % close to the theoretical value [7].

For synchrotron radiation optics and applications in X-ray astronomy, high thermal and long term stability of the multilayer systems is desirable. The thermal stability of Mo/Si multilayers deposited with sputtering has been investigated in a number of works [8-14]. The general results is that these multilayers are destroyed already at temperatures of around 400 °C. The Mo/Si multilayer referred to in figure 1, produced by a very slow e$^-$-beam deposition rate of 0.005 nm/s and thermal treatment during deposition, loses its normal incidence reflectivity at temperatures higher than 500 °C completely. Thus Mo/Si multilayers cannot serve as mirrors of the direct undulator beam of storage rings because of too high temperatures. In order to overcome this temperature limit, the Mo layers have been mixed with Si to get a Mo$_{0.5}$Si$_{0.5}$/Si multilayer since the interdiffusion rate as a mechanism of destruction of the layer structure is then strongly reduced. This replacement of Mo by Mo$_{0.5}$Si$_{0.5}$ reduces however the normal incidence reflectivity in the low temperature range from 60 % to 47 % as given in figure 1 (solid curve), but the multilayer now serves as an X-ray mirror up to temperatures of 900 °C as shown in figure 2 [6]. After baking at 600 °C the reflectivity is decreased to 15 % at 13 nm and remains almost constant up to 850 °C. Large angle X-ray scattering (LAXS) studies as well as TEM studies of the samples reveal the development of MoSi$_2$ crystallites at temperatures of 600 °C and higher. This is certainly at least partly responsible for the abrupt changes in reflectivity and double-layer thickness between 500 °C and 600 °C, given by the upper and lower part of figure 2, respectively [6].

Besides the use of X-ray diffraction (normal and grazing incidence) as well as of microscopic techniques (TEM, STM and AFM), the multilayer systems have been analyzed with respect to their microstructure by means of surface physics techniques such as sputtering,
in combination with mass analysis of ejected particles (SNMS) as well as Auger electron spectroscopy (Sputter/AES) and the non-erosive Rutherford Backscattering (RBS) [15, 16, 7].

Figure 3 shows RBS-spectra (energy distribution of backscattered He\(^+\) ions) measured with an electrostatic analyzer with an energy resolution \(\frac{\Delta E}{E}\) of \(5 \times 10^{-3}\) [17]. For the Mo/Si layer system with \(N = 12\) double layers and a double layer thickness of \(d = 7\) nm, the spectra in the left part of figure 3a allow a determination of the Mo- and Si-concentration in a layer-resolved manner. The multilayer was baked for 20 minutes at 500 °C and 600 °C in vacuum in order to observe the changes in the material distribution. The backscattering spectra obtained after baking are displayed in the middle of figure 3. Baking at 500 °C hardly has an effect on the material composition in the stack. Only a slight damping of the oscillations in the spectra is observed. After heating to 600 °C both the oscillations in the energy distribution of the Mo and Si part of the spectra have vanished. A shift to higher energies is observed for the high energy edge of the Mo part, while the intensity at the high energy edge of the Si part is reduced. These two facts are compatible with an interdiffusion of the Mo and Si layers. No redistribution of material over the whole stack is observed. The total intensity of backscattered particles in figure 3a changes neither for the Mo part nor for the Si part, indicating that no material is lost during the baking procedure.

The spectra in the right part of figure 3b which were measured for a geometry with good depth resolution yield additional information about the individual interfaces: for the sample
Fig. 3. — Backscattering spectra for a Mo/Si multilayer fabricated at 150 °C with and without baking at temperatures of 500 °C and 600 °C. Two different geometries have been chosen: geometry a) with normal ion incidence and an exit angle of 32° provides good mass resolution, geometry b) with 30° ion incidence and an exit angle of 70° provides good depth resolution. The inset (bottom) shows the spectrum for the non-baked sample with an expanded energy scale. The arrows in the middle part indicate the energies expected for Mo and Si for backscattering from the surface [17].

which was deposited at 150 °C the slope of the high energy side of the Mo-peaks is larger than the slope at the low energy side (see also inset with enlarged energy scale at the bottom of Fig. 3). This is due to interfacial layers with different thicknesses at the Mo on Si and the Si on Mo interfaces [17].

Further investigations concerning the influence of the deposition temperature on multilayer systems were carried out by means of Sputter/AES-depth profiling. Sputtering was performed by means of 600 eV Ne ions which turned out to be the best projectiles for achieving a high-depth resolution in the sputter removal process. In figure 4 the AES-signals for a Mo/Si multilayer deposited at 30 °C show less pronounced oscillations than those for 150 °C, indicating a better separation of the individual layers for 150 °C [7, 16]. For the 30 °C-system
2. Multilayer coated X-ray diffraction grating.

High efficiency and high resolution soft X-ray optics operating at normal incidence can be obtained by developing a multilayer with a periodic lateral structure. The main advantages of these optical elements are high efficiency due to the multilayer coating, coupled with high spectral resolution provided by the grating structure. Most publications [18, 19] deal with laminar amplitude gratings, which cause diffraction by varying the amplitude across the impinging wavefront due to scattering and non-scattering surfaces. For an ideal type of grating, 25% and 10% of the coating reflectivity is diffracted in the zeroth and first order, respectively. Higher diffraction efficiencies can be expected for a two-surface laminar phase grating, where the phase relationships in the diffracted wavefront are controlled by the multilayer period thickness and the grating groove depth. A complete cancellation of the zeroth order is possible if the path difference of waves diffracted from the lands and the grooves is an odd multiple of $\lambda/2$, while the diffraction efficiencies in the first order can reach 40% of the coating reflectivity. It is worth noting that we have obtained better results for multilayer gratings where the multilayer is deposited on a grating preshaped than where the grating is etched into a predeposited multilayer, since they are of different type: phase and amplitude gratings, respectively.

Figure 5 shows the set up of a laminar phase grating consisting of a laterally structured Si-wafer which is coated with a Mo/Si-multilayer [15, 20, 21]. The 2400 l/mm laminar
The multilayer-coated diffraction grating and the geometry for its soft X-ray optical characterization.

A multilayer grating [21] has been fabricated by Zeiss using holographic lithography followed by ion beam etching and plasma-ashing. The desired land-to-groove ratio is 1:1, the groove depth being 20 nm. The grating substrate is coated with a Mo/Si-multilayer of 12 periods and a period thickness of 8 nm. Normal incidence reflectivities of multilayer mirrors of this kind have been measured to be about 30 % at $\lambda = 15.5$ nm. The optical performance of the multilayer grating has been characterized by use of synchrotron radiation in the 12-18 nm wavelength range. The normal incidence specular reflectivity versus wavelength is shown in the top part of figure 6, the Bragg reflectivity maximum is reached at $\lambda = 15.6$ nm [15, 21]. The grating diffraction efficiencies measured at a constant wavelength of 15.6 nm are displayed in the bottom part of figure 6. 5.5 % of the incident beam intensity in both the +1st and −1st grating diffraction order, which is about 50 % of the theoretical value for an ideal laminar phase grating (i.e. one with optimum matching of multilayer and grating structure) is measured, while only 4.5 % are obtained in the 0th order.

The surface topography of the multilayer grating investigated by SEM is shown in figure 7 [21], which shows a land-to-groove ratio of 0.4:0.6, as well as unequal surface roughnesses of the lands and the grooves. These imperfections result in unequal scattering amplitudes. The incomplete cancellation of the zeroth order has been explained quantitatively by an effective amplitude ratio of 0.35:0.65 [21], and the fact that the grating diffraction is additionally reduced by a non-ideal grating profile, which tends to have a more sinusoidal shape (concluded from the AFM-scan of the coated grating).

The diffraction efficiencies in the +1st diffraction order measured between $\lambda = 15-16$ nm are displayed in figure 8 [21] and show a maximum at $\lambda = 15.6$ nm, which is the wavelength of the multilayer reflectivity maximum. The coincidence of multilayer reflectivity maximum and grating diffraction efficiency maximum is significant for the good matching of the multilayer and grating structure.

3. Multilayer mirror laterally structured by RIE as mask for soft X-ray projection lithography.

The future development of microstructure technology requires the production of structures with dimensions smaller than those attainable by optical lithography (about 0.25 μm) [22, 23].
There are various possibilities to advance towards nanolithography, i.e. to obtain structure sizes in the sub-0.1 μm range.

A complementary technique to transmission lithography 1:1 X-ray proximity printing is soft X-ray projection lithography (SXPL) [24-28]. Imaging X-ray optics may perform a demagnification and hence the smallest structures necessary on the mask have sizes easily attainable by standard optical lithography. In connection with X-ray reflection masks this technique has the principal advantages of high thermal and mechanical mask stability due to the thick substrate. A reflection mask is a multilayer mirror consisting of areas with high reflectivity and areas where the reflectivity is as low as possible (close to zero) yielding the expected high contrast (~10^4). The reflecting parts represent the structure desired for the imaging.

There are two different methods of fabricating the mask, both using the standard techniques of microfabrication developed for microelectronics. The first one uses an additional absorbing layer placed where the mask should not reflect. The contrast is then determined by the
Fig. 7. — SEM of the multilayer coated X-ray grating [21].

Fig. 8. — Diffraction efficiencies in +1.0 order, $\alpha + \beta = 2'$ (N.1) [21].
thickness and the absorbing coefficient of the covering material. In this case the contrast is the square of that of a comparable transmission mask since the light travels twice through the absorber and is smaller than the contrast of the second technique shown in figure 9 [26] and described in the present paper. Here the non-reflecting areas are obtained by removing the multilayer by the process steps illustrated as follows: a photoresist (Hoechst AZ 4210) 3.2 μm in thickness is spin coated onto the multilayer and patterned by photolithography. Using the photoresist as an etch mask the pattern is transferred to the multilayer by reactive ion etching (RIE) using pure CF₄. The RIE process was performed in a Leybold Heraeus Z 401S (parallel plate reactor with graphite electrodes) with a plasma generating electrical power of 27W and CF₄ pressure and a flow of 1Pa and 10 standard cm³/min (sccm), respectively. The etching time was estimated from known etching rates in order to remove the multilayer down to the Si-substrate. After RIE the remaining photoresist was removed with acetone without damaging the structured multilayer. The etching depth was measured with a profilometer and turned out to be sufficient after an etching time of 50 min for a 2 d = 15 nm multilayer, resulting in etching rates for silicon and molybdenum of \( R_{Si} = (4.7 \pm 0.7) \) nm/min and

![Figure 9](image-url)

Fig. 9. — Step-by-step illustration of the reflection mask fabrication using optical lithography and reactive ion etching (RIE) of a multilayer, as explained in the text [26].
$R_{Mo} = (1.6 \pm 0.4)$ nm/min, respectively. An optical microscope photograph of part of a reflection mask produced this way is shown in figure 10.

In a first test of the X-ray reflection mask a very simple set-up without imaging optics was used as shown in figure 11 [26]. The reflection mask was mounted in the first mirror holder of a double crystal monochromator. The mask was illuminated by white synchrotron radiation at the beamline BN2 of the Bonn University electron accelerator ELSA, operated in storage ring mode with an electron energy of 2.3 GeV and an average current of 40 mA. The entrance slit of the monochromator was opened as wide as possible, giving an illuminated spot size of $10 \text{ mm(H)} \times 5 \text{ mm(V)}$. An angle of incidence of $30^\circ \pm 0.5^\circ$ at the multilayer mask was chosen. Due to the monochromator design, the light reflected was s-polarized. It exposed the Hoechst AZPF514 positive X-ray resist coated on a Si-wafer substrate which was mounted perpendicular to the reflected beam as shown in figure 11. This guaranteed a maximum power incidence onto the resist. The resist was developed for the white spectrum of the BESSY storage ring in Berlin running at $754 \text{ MeV}$. Under these conditions an incident energy density of 30 to $75 \text{ mJ/cm}^2$ was recommended by the producer. In the experiment discussed a 1.1 $\mu$m thick resist spin-coated onto a Si-wafer was used. This is thick enough to absorb nearly all the radiation reflected by the mask in the energy region around $100 \text{ eV}$, in contrast to the BESSY spectrum which is only partly absorbed. Thus the absorbed energy necessary for optimal exposure was lower than the values indicated by Hoechst. A microscope photograph of the
irradiated resist (developed by a 150 s immersion in AZ 400K diluted 1:4 with water) is shown in figure 12, lower part.

The energy necessary for a full exposure of the resist can be calculated from the incident synchrotron radiation, the mask reflectivity and the resist absorption. Assuming the resist absorption at a photon energy of 100 eV to be very close to one, the reflectivity of the mask as that determined by the reflectivity measurements of the original multilayer mirror, and using the calculated spectrum of the incident radiation, best results were obtained with a deposited energy of \((6 \pm 2.5)\) mJ/cm².

With the experimental set-up as given in figure 11, the accuracy of the image of the structure in the resist is limited by Fresnel diffraction. The Fresnel diffraction is negligible if the slit width (i.e. the multilayer mask line width) \(B\) is large compared to the scale factor \(F = \sqrt{D \lambda / 2}\) (with \(D = \) distance mask — resist perpendicular to the mask) defining the resolution limit. The images produced have been made at a distance \(D\) of about 6 mm resulting in \(F \approx 6\) μm. The Fresnel diffraction figure observed on the resist was calculated and displayed in figure 12, upper part [26]. The dotted line represents the geometrical shadow. On the same scale the lower part of figure 12 shows the structured resist. The agreement between the observed and the calculated diffraction pattern is obvious, showing an experimental resolution of 8 μm [26].

The results shown demonstrate that the Fresnel diffraction was the limiting source of inaccuracy of imaging and not the divergence of the radiation used or any other reason. In other words, if the Fresnel diffraction is excluded in a projection setup by means of demagnifying focussing X-ray mirrors, as demonstrated by reference [27] for the first time, laterally structured multilayer mirrors will successfully serve as reflection type masks for large area projection lithography and obtain structure sizes in the sub 0.1 μm range. Reference [27] has already done this with an area of 2 mm × 0.6 mm and an accuracy of 0.25 μm.
Fig. 12. — Fresnel diffraction of the reflection mask line pattern. Top: calculation with $\lambda = 124$ Å and $D = 6$ mm (dotted line = geometrical shadow). Bottom: photograph of the equivalent sample [26].

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