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Thermal Stability of Mo/Si Multilayer Soft-X-Ray Mirrors Fabricated by Electron-Beam Evaporation

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Abstract. Mo/Si multilayers are fabricated by electron-beam evaporation in UHV at different temperatures (30° C, 150° C, 200° C) during deposition. After completion their thermal stability is tested by baking them at temperatures (T_{bak}) between 200° C and 800° C in steps of 50° C or 100° C. After each baking step the multilayers are characterized by small angle Cu_{K_α}-X-ray diffraction. Additionally, the normal incidence soft-X-ray reflectivity for wavelengths between 11 nm and 19 nm is determined after baking at 500° C. Furthermore, the layer structure of the multilayers is investigated by means of Rutherford Backscattering Spectroscopy (RBS) and sputter/Auger Electron Spectroscopy (AES) technique. While the reflectivity turns out to be highest for a deposition temperature of 150° C, the thermal stability of the multilayer increases with deposition temperature. The multilayer deposited at 200° C stands even a 20 min 500° C baking without considerable changes in the reflectivity behaviour.

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In the wavelength range between 13 nm and 30 nm the combination of Mo and Si is most widely used for normal-incidence multilayer mirrors. Reflectivities around 60% have been achieved with both sputtering [1] and e^--beam evaporation in combination with thermal treatments during deposition [2,3]. Besides a high value for the reflectivity, the stability of the multilayer stack is also an important property, since applications include for example synchrotron radiation optics, where the multilayer can be heated to a few hundred degrees Celsius [4]. The long-term stability is also important for a number of applications.

The thermal stability of Mo/Si multilayers has been studied earlier in several works [5–11] but in all of them the multilayers are fabricated by sputtering. In [12] it is shown that thermal treatment during e^--beam deposition can considerably enhance the reflectivity of Mo/Si multilayer mirrors with a double layer spacing of about 7.5 nm. For a deposition temperature (T_{dep}) of 150° C the reflectivity is about a factor of two larger than the reflectivity of the 30° C and 200° C sample [12, 13]. In other previous works [14, 15] the influence of the deposition temperature on the microstructure of Mo/Si-multilayer systems fabricated by e^-- beam evaporation was studied. They have shown that Mo/Si multilayers have interlayers of a mixture of Mo and Si at the Mo-Si interfaces and that the thickness of Mo- on- Si interlayers increases with increasing deposition temperature, while the thickness of the Si- on- Mo interlayers keeps constant. In our work the influence of the different microstructure for the multilayers which were deposited at different temperatures on the thermal stability is also investigated.

1 Experiment

In this work we study the thermal stability of Mo/Si multilayer mirrors which are e^--beam deposited at 30° C, 150° C and 200° C. The multilayers are fabricated in ultra high vacuum with two e^--beam evaporation sources, one for Mo and one for Si. The distance between the substrates and the evaporation sources is around 65 cm. The deposition system possesses two quartz oscillators for measurements of deposition rate and layer thickness. The layer thickness is controlled by an in situ reflectivity measurement with Cu_{K_α}-radiation ($\lambda = 4.47$ nm) at an angle of $\alpha = 70°$ with respect to the surface normal of the substrate. The substrates can be heated with a tungsten filament. T_{dep} is measured at the substrate holder with a NiCr/CuNi thermocouple. The base pressure of the system is around 1×10^{-8} Pa and typical pressures during deposition are about 1×10^{-6} Pa. The deposition rates are 0.06 Å/s for Mo and 0.02 Å/s for Si. As substrates Si (100) wafers were used. All the results described in this work are obtained for multilayers with 12 double layers and a double layer with a thickness (d-spacing) of about 7.5 nm. The nominal thickness was about 2.5 nm for Mo and 5 nm for Si. The samples are baked to temperatures between 200° C and 800° C in steps of 50° C or 100° C. The baking is done under vacuum (5×10^{-3} Pa) for 20 min at each

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temperature. The temperature is measured at the substrate holder with a NiCr/CuNi thermocouple. After each baking step the samples are characterized by measuring the small angle X-ray reflection with a Cu_{K_α} line source. The material distribution of the as deposited X-ray mirrors fabricated at different temperatures is studied with sputter/AES-depth profiling. Sputtering was performed by means of 600 eV Xe ions. The depth resolution is 1 nm. Additionally, the baking induced changes in the material distribution of the multilayer deposited at 150° C are investigated by means of high-resolution RBS. These measurements were carried out by use of a He^+ beam provided by a 350 keV ion accelerator. The energy of the backscattered ions is determined using a toroidal electrostatic analyzer. These characterization methods give information about the *d*-spacing, interfacial roughness, formation of interfaces and thickness errors, and thus, especially about the general quality of the stack. In addition, the diffusion processes that have occured during thermal treatments can be observed. Further details about the fabrication and characterization procedures are given in [16]. The normal-incidence reflectivity for soft X-rays is determined in the spectral region of 11–19 nm using a reflectometer at the electron storage ring BESSY [17].

2 Results

2.1 Sputter/AES-Depth Profiling

The distribution of the material within the stack for the as deposited mirrors was investigated by sputter/AES-depth profiling. The ratio of intensities I/I_{max} for Mo and Si versus the sputter depth are given in Fig. 1 for the multilayers deposited at 30° C, 150° C and 200° C. The AES signals of Si for 30° C and 200° C deposition temperature show lower oscillations than for 150° C. The peaks of the AES signals are asymmetric, which is less pronounced for the 30° C system than for the stacks of higher deposition temperature. The more symmetric peaks of the layers deposited at 30° C indicate similar interfaces for both the Mo- on- Si and the Si- on- Mo side, the shallow slopes combined with lower Si oscillations are in agreement with rather rough interfacial regions. The asymmetric form especially for the Mo signal of the 150° C and 200° C stacks indicates sharper interfaces on the Si- on- Mo side than on the Mo- on- Si side, the steps in the slopes can be caused by interface layers. These results are in agreement with [14, 15]. For the 200° C system the Si signal does not drop to values near zero. This can be explained by interdiffusion of Si and Mo, which leads to layers which are not as well separated as for the 150° C stack.

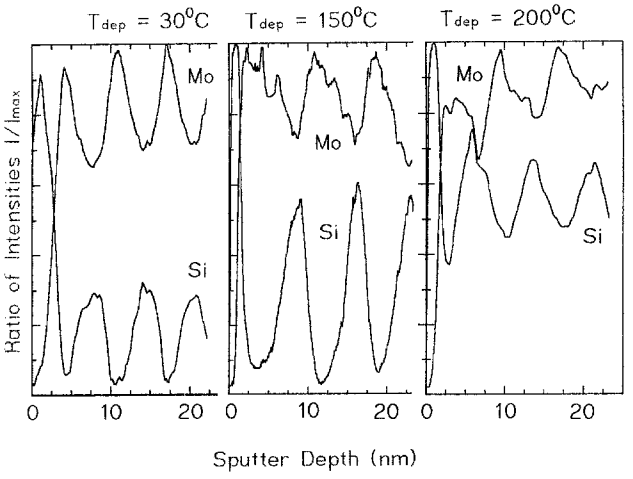

Fig. 1. Mo and Si peak heights in sputter/AES-depth profiles for as-deposited multilayers deposited at different temperatures

2.2 Small-Angle X-Ray Scattering

Figure 2 shows a series of Cu_{K_α} reflectivity curves obtained for a multilayer which is deposited at 150° C. The reflectivity curve of the as deposited sample was measured up to the fourth Bragg order. The baking procedure does not induce significant changes in the reflectivity behaviour up to temperatures of 400° C, as can be seen in Fig. 2. After baking to 500° C the first-, second- and third-order Bragg maxima are located at larger angles Θ and the intensity ratio

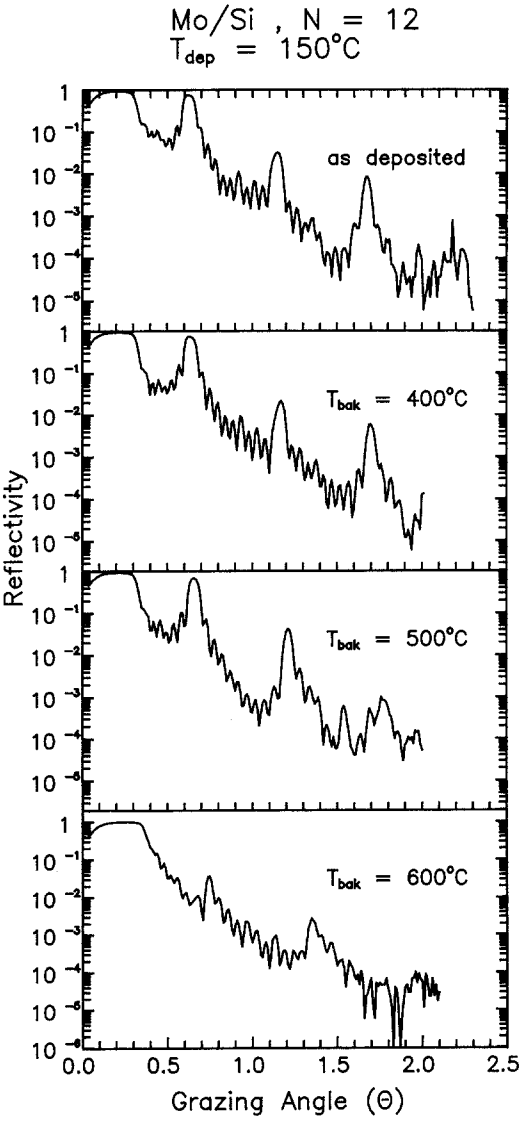

Fig. 2. Small angle Cu_{K_α} X-ray diffraction of the multilayer deposited at 150° C directly after completion (30° C) and after baking at 400° C, 500° C and 600° C

between the second- and third-order Bragg peak has changed considerably. The former finding is due to a change in d-spacing [10] while the latter can be explained by a change in the ratio of absorber (Mo) and spacer (Si) thickness [12]. Baking to 600° C yields a drastic decrease of the reflectivity of the first-order Bragg peak and a further considerable shift of the Bragg maxima to larger Θ. A pronounced second-order Bragg peak remains visible; this indicates that the reduction in reflectivity of the first-order Bragg peak is rather due to a thickness reduction of the silicon spacer layer by diffusion than due to a thermally induced roughening of the interfaces, because thermally induced roughening of the interfaces reduces the reflectivity of the higher Bragg orders more than the reflectivity of the lower [7]. This qualitative picture is further supported by a more detailed study of the first- and second-order Bragg maxima-intensities and -positions, which are displayed in Fig. 3. Open circles represent the results of the stack deposited at 150° C, crosses and open squares those for deposition at room temperature and at 200° C. The first-order Bragg peak intensity (Fig. 3a) remains almost constant for all samples up to a certain temperature and decreases then drastically with increasing temperature. The breakdown of the reflectivity occurs for our samples deposited at room temperature, 150° C and 200° C, around 450° C, 550° C and 500° C, respectively.

Figure 3b, c gives a hint on the mechanism that produces the different stability of the samples deposited at different temperatures. The second-order Bragg peak intensities relative to the intensity of the as deposited mirrors for the three e^--beam deposited samples versus baking temperature are given in Fig. 3b. For all samples the intensity remains constant at temperatures below 300° C. Intensity changes are observed around 400° C and for all samples the intensity increases considerably at a baking temperature directly below the temperature at which the intensity of the first-order Bragg peak breaks down (see Fig. 3a). The changes of d-spacing (Δd) of the different stacks versus baking temperature are given in Fig. 3c. They are deduced from the angular positions of the third-order Bragg maxima using a program that corrects for the refraction index of the multilayers. No changes are observed for baking temperatures below 300° C. At higher baking temperatures significant changes in Δd are observed for all samples, but the baking temperatures at which the most significant changes in Δd occur are identical with those at which the reflectivities of the first-order Bragg maxima break down (Fig. 3a).

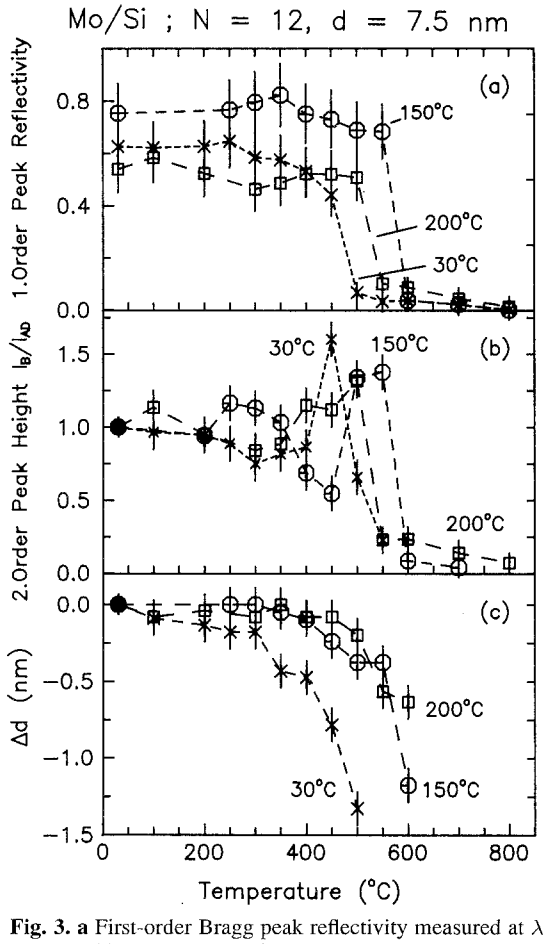

Fig. 3. a First-order Bragg peak reflectivity measured at $\lambda = 0.154$ nm versus baking temperature for the mirrors deposited at 30° C (*crosses*), 150° C (*open circles*), 200° C (*open squares*). **b** Second-order Bragg peak height versus baking temperature for the same e^--beam deposited multilayers as in **a**. The peak heights (I_T) are normalized to the values of the As Deposited (I_{AD}) mirrors. **c** Δd deduced from the angular positions of the third-order Bragg maxima versus baking temperature for the same e^--beam deposited samples as in (**a**) and (**b**)

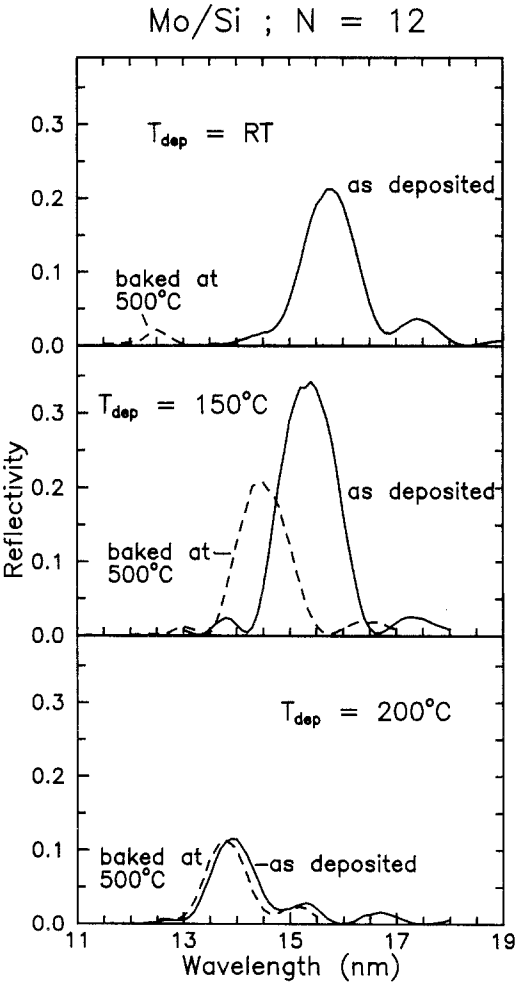

Fig. 4. Normal-incidence soft-X-ray reflectivities versus wavelength of the as-deposited multilayer mirrors (*solid curves*) and after baking at 500° C (*dashed curves*). The curves in the *upper*, *middle* and *lower* part of the figure were obtained for multilayers deposited at 30° C, 150° C and 200° C, respectively

2.3 *Reflectivity Measurements with Synchrotron Radiation*

Directly after the deposition and after the 500° C baking process the multilayers are characterized with synchrotron radiation in the wavelength range between 11 nm and 19 nm. Figure 4 shows normal incidence reflectivity curves for the three different multilayers with 12 double layers fabricated at room temperature, 150° C and 200° C. Deposition at 150° C yields the highest normal incidence reflectivity of about 35%. The reflectivities in this work are lower than those in [2, 3] because the number of double layers $N = 12$ is lower than in [2, 3] ($N = 30$). The reflectivities of the room-temperature- and the 200° C-sample are smaller by more than a factor of 2. After the 500° C baking the stack deposited at room temperature is almost completely destroyed. For the multilayer deposited at 150° C the reflectivity curve versus wavelength changes in both the maximum intensity and the peak position when baking at 500° C is performed but the peak reflectivity is still larger than 20%. For the sample deposited at 200° C the 500° C baking turns out to have practically no effect on the reflectivity behaviour.

2.4 *High-Resolution* RBS

Additionally, the layer structure of the multilayers was studied for the as-deposited multilayers and after 20 min baking at 550° C and 600° C with high-resolution RBS (5×10^{-3}) [18]. Figure 5 shows the backscattering spectra (intensity measured by the analyser versus backscatter energy) for the sample deposited at 150° C obtained with 350 keV He^+ ions. The spectra in Fig. 5a, b were measured in different scattering geometries. The measuring geometry for (a) was normal ion incidence and an exit angle of 32°. This provides high mass resolution. The spectra in (b) were measured with an incidence angle of 21° and an exit angle of 77°, both with respect to the surface normal. This results in a good depth resolution. In Fig. 5a the signals of Mo and Si are separated. For the as deposited mirror the signals for both materials show a number of oscillations, which represent the backscattering from the individual layers in the stack. The thickness errors in this layer system are obviously very small ($< \pm 10\%$). After baking for 20 min at 550° C the deepness of oscillations in the spectrum is slightly reduced. At a baking temperature of 600° C the oscillations have almost vanished. A shift to higher energies is observed for the high-energy edge of the Mo part of the spectrum. These two facts are compatible with an interdiffusion of the Mo and Si layers. The total amount of material does neither change for Mo nor for Si with increasing baking temperature. Therefore, it can be concluded that the change of d-spacing with baking (Fig. 3b) is exclusively due to a higher atomic concentration of the materials within the stack. A measurement with an enhanced depth resolution gives hints of the formation of Mo-Si interlayers (Fig. 5b). The spectra in Fig. 5b shows the backscattering from the uppermost two Mo layers for the as deposited sample and after baking at 550° C and 600° C measured in a scattering geometry which provides good depth resolution. The shape of the Mo peaks is asymmetric. The slope of the Si- on- Mo (right) side of a Mo peak is higher than the slope of the Mo-on- Si (left) side. This is a further hint that at the Mo- on- Si interfaces larger Mo/Si interlayers exist than at the Si- on- Mo interfaces, if the multilayer was thermally treated during deposition [14, 15]. The slope on the low energy side of the first Mo peak below the surface (Mo- on Si- interface) exhibits a slight shoulder located in the upper region of the decrease. By simulating the RBS spectrum for a given layer system (shown by the dashed curve in Fig. 5b) this shoulder

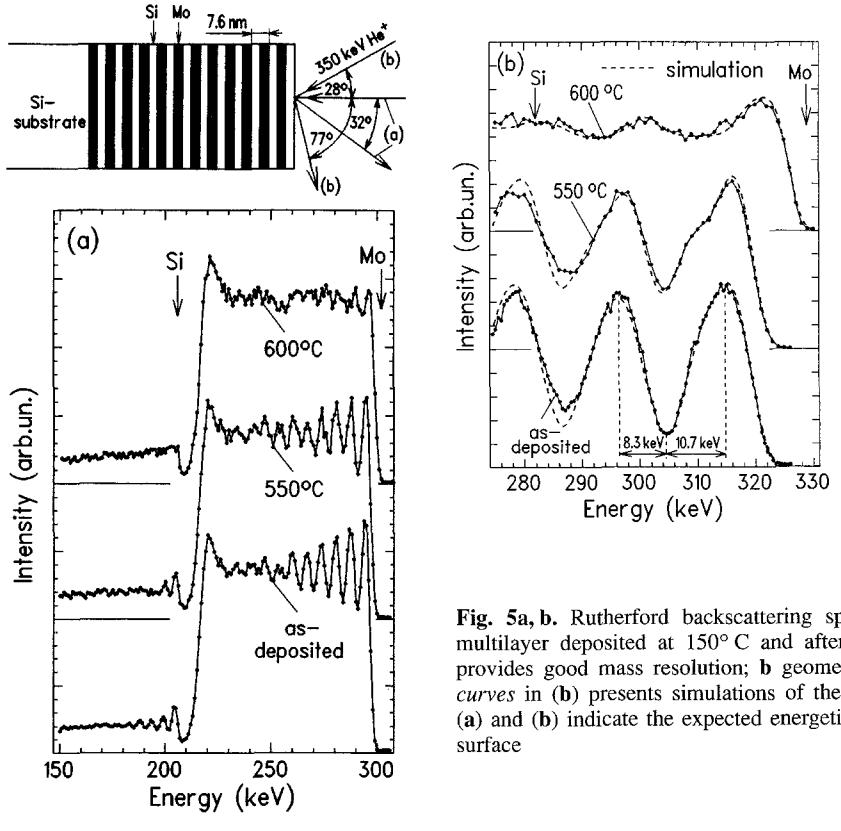

Fig. 5a, b. Rutherford backscattering spectra obtained with an electrostatic analyzer for the multilayer deposited at 150° C and after baking at different temperatures. **a** Geometry which provides good mass resolution; **b** geometry which provides good depth resolution. The *dashed curves* in (**b**) presents simulations of the RBS spectra for a given layer system. The *arrows* in (**a**) and (**b**) indicate the expected energetic positions for ions backscattered from Si or Mo at the surface

can only be produced by use of a Mo-rich mixed interlayer at the Mo- on Si- interface. After baking at 550° C the deepness of the Mo oscillations is clearly reduced. The major change compared to the as-deposited sample has occurred at the Mo- on Si-interface, whereas no change in the spectrum at the high-energy side of the first Mo peak (Si- on Mo-interface) is detectable. Therefore, the interdiffusion starts mainly at the Mo- on Si-interface. At this interface a larger shoulder has developed. This shows that the thickness of the interlayer has increased considerably with baking. A simulation of the spectrum after baking at 550° C yields a Si/Mo atomic ratio in the interlayer close to one. After baking at 600° C the oscillations have almost vanished, showing that strong interdiffusion has occurred. Only slightly Mo-richer regions exist in the sample, which might be the residue of the originally pure Mo layers. The simulation of this spectrum yields a Si/Mo atomic ratio about 1.7 for the Si-rich regions.

3 Discussion

In order to explain the different thermal stability of the three samples, which were fabricated at 30° C, 150° C and 200° C, we must consider the different microstructure of the multilayers deposited at different temperatures. In [12] it was shown that thermal treatment during deposition yields smoother interfaces than deposition at room temperature. Slaughter et al. [14] and Stearns et al. [15] have obtained two kinds of interlayers of amorphous Mo silicides. The thicknesses of the Mo- on- Si interlayers increase with increasing deposition temperature. The thicknesses of the Si-on- Mo interlayers remain constant for deposition temperatures between 30° C and 300° C. In consideration of this the data presented in Figs. 1–5 are compatible with the following model.

Deposition at room temperature produces multilayers with a large interface roughness due to a suppression of surface diffusion. Thermal treatment to 150° C during deposition yields an enhanced surface diffusion [14, 15], smoother interfaces [12] and thicker interlayers of Mo silicides, which were observed with sputter/AES and RBS measurements in agreement with [14, 15]. In these stacks the concentration gradient for Si is smaller than for the multilayers deposited at room temperature. The reflectivity of the stacks is then the highest and the films have a higher stability than room temperature deposited films. Deposition at 200° C yields broader interlayers and d-spacing errors in the stack (this was concluded from the fact that deposition at 200° C yields considerably broader Bragg peaks in the Cu_{K_α} reflectivity), which may result from variations of the interface diffusion of Mo and Si within the stack. Thus the reflectivity is lower, but the stability of this stack is higher.

In Table 1 we compare the thermal stability of our mirrors deposited by e^--beam evaporation with the thermal stability of multilayers, which were fabricated by sputtering. The temperature at which the reflectivity of the first order Bragg peaks break down for these mirrors are lower than the baking temperature for our mirrors, which were e^--beam deposited and thermally treated during deposition. In the literature activation energies E_a for diffusion were deduced by means of an Arrheniusplot of the multilayer d-spacing $\ln(\Delta d)^2$ versus 1/baking temperature [6, 10, 11]. The RBS spectra in Fig. 5b show, that for our multilayers the composition of the interlayers changes during baking. In consideration of this an Arrheniusplot on the basis of Cu_{K_α}-reflectivity data, which implies a constant ratio of Si to Mo in the interlayers with baking, is not applicable, because the change in d-spacing is no longer proportional to the amount of the diffused material.

4 Conclusion

We have studied the thermal stability of Mo/Si multilayers which are produced by e^--beam evaporation in UHV and thermal treatment during deposition. In addition to the earlier finding [12] that thermal treatment during deposition can yield a significant increase in the reflectivity of the multilayer this work shows that thermal treatment during deposition has also a considerable effect on the stability of the multilayer. Those multilayers which are produced at the highest deposition temperature, i.e. at 200° C in this work, have only a comparatively low peak reflectivity of about 12% with 12 double layers, which is the half of the

Table 1. Mo/Si multilayer stability for sputtering (data from literature) and e^--beam deposition (this study). The table list values of the maximum baking temperature T_{max} at which the reflectivity of the first-order Bragg peak for Cu_{K_α} radiation (Rosen et al. give only values for soft X-ray radiation) remains larger than 0.2 of the reflectivity of the as deposited sample

Reference	Baking duration [min]	d-spacing [nm]	Baking steps [° C]	T_{max} [° C]	Measurement technique	E_a [eV]	Temperature range for E_a [° C]
Nakajima et al. [10]	53	7.63	50	400	SAXS	1.1	400–600
Jiang et al. [5]	30	11.87	100	400	SAXS	–	–
Holloway et al. [6]	0.5	13	50	–	SAXS	2.0	400–500
Stearns et al. [7]	30	11	200	400		–	–
Fedorenko et al. [9]	120	8	100	320		–	–
Rosen et al. [11]	60	7	100	298	TEM	1.2	225–400
					SAXS		
This study							
$T_D = 30°$ C	20	7.7	50	450	SAXS	–	–
$T_D = 150°$ C	20	8	50	550	SAXS	–	–
$T_D = 200°$ C	20	7.2	50	500	SAXS	–	–

multilayers deposited at 150° C, but they are showing the best stability.

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