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Sc–Si normal incidence mirrors for a VUV interval of 35–50 nm

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Abstract

The Sc/Si multilayers are suggested as high-reflectivity coatings for a VUV interval of 35–50 nm. Fabricated mirrors show the normal incidence reflectivity of 30–50% which is high enough to effectively manipulate the beams of synchrotron radiation and compact discharge and laser-driven X-ray lasers. The obtained values are not, however, limiting for the Sc/Si coatings. Theoretical estimations as well as electron microscopy studies of Sc–Si interfaces indicate a large potential for further raising the reflectivity. © 2000 Elsevier Science B.V. All rights reserved.

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In spite of impressive progress in X-ray and VUV optics there is a spectral range where the normal incidence optics cannot still be used in SR research as well as in other applications, such as X-ray lasers, astrophysics, microanalysis, etc. This region, which is placed between 35 and 50 nm, has too short wavelengths for bulk mirrors and too long wavelengths for known multilayer mirrors and therefore is difficult for the coating design. The interval under consideration lies just between a long wavelength region where optical spectra of solids are formed by excitations of valence electrons and a short wavelength region where excitations of core electrons are of crucial importance. Neither Al and LiF, which are the key components of reflectors at $\lambda > 100$ nm nor Mo/Si multilayers, which are widely used at $\lambda = 13$–30 nm can be applied to this spectral interval [1]. It should also be mentioned that the highest normal incidence reflectivity found for bulk materials ranges from 20–25% at 50 nm to 8–5% at 35 nm (Ir, Os) [2,3]. Theoretical estimations based on optical constants [2] predicted that Os/Si, Ir/Si, Os/Al and Ir/Al multilayers can show the reflectivity of 30–35% [4]; however, only the reflectivity of 20% at 38 nm was obtained in the synthesized Os/Si coatings [4]. Since these values are not sufficient for applications, the burning problem is to select materials for high-reflectivity coatings which are effective at these wavelengths. Our recent study of the Sc/Si [5] multilayers showed a large potential of this system. This paper presents our argumentation in favour of

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this choice of partner materials, the detailed description of multilayers preparation and the results of reflectivity measurements. The microstructure and the chemical composition of layers, which are of key importance for coating reflection are carefully studied by the methods of X-ray diffraction, X-ray microanalysis and cross-sectional electron microscopy.

Efficiency of the search for a good material combination is directly linked to the currently available information about optical constants of solids. The optical properties of only a few materials have been measured at $\lambda = 35$–50 nm [2]. Several of them have low absorption at wavelengths of interest, hence the choice of a spacer material creates few problems. We picked silicon by reason of large experience gained in Si layer deposition. The search for a partner material having the largest Fresnel reflection at the boundary to Si is, however, much more difficult. Published experimental data provide no good candidate for this purpose. Under these circumstances additional information about optical constants of solids is of decisive importance. To obtain it, we turned to the results of ab initio calculations of optical spectra in the 3d-, 4d- and 4f-transition metals at photon energies $\hbar\omega = 0$–60 eV [6–8] and studied trends in the Periodic Table. Such a broadening of the search allowed us to pick Sc as the best partner of Si. It was found out that scandium has the highest refractive and the lowest absorption indices among the transition metals. This extreme behaviour of refraction and absorption at wavelengths of interest has dissimilar origins. The main contribution to the refractive index originates from very intense transitions of the 3p- core electrons to the practically unoccupied 3d-band of Sc. These transitions are characterized by the photon energy $\hbar\omega_c = 37$ eV and the oscillator strength $f_c = 5$. They start just near the short-wavelength boundary of the interval under consideration. Inside the interval the dielectric function of Sc can be approximated as

$$\varepsilon(\omega) = 1 - \frac{N_v \Omega_p^2}{\omega^2} + 2i\beta_v(\omega) + \frac{f_c \Omega_p^2}{\omega_c^2 - \omega^2 - i\delta} \quad (1)$$

where N_v is the number of valence electrons which is equal to 3 for Sc, $\beta_v(\omega) \approx 0.05$, $\Omega_p^2 = 4\pi e^2/mV$ and V is the atomic volume. It should be noted that the value $\mathrm{Im}\,\varepsilon(\omega) = 2\beta_v(\omega)$ originates only from excitations of valence electrons and hence is proportional to N_v. Being a beginning element of the 3d-series, scandium has a small number of valence electrons and therefore low absorption. Another reason for low absorption is a large atomic volume of Sc, which is half as much as the volume of other 3d-metals. Expansion of the volume considerably reduces the energy scale for excitations of valence electrons and thereby causes nearly full exhaustion of these excitations at $\lambda = 35$–50 nm.

The perfect combination of excitations of valence and core electrons makes scandium the most promising element for coatings intended for wavelengths $\lambda = 35$–50 nm. To check this proposition, we calculated the normal incidence reflectivity of several Sc/Si multilayers using the characteristic matrix method. Optical constants of Sc and Si were taken from the ab initio calculations [6] and from the handbook [2]. The calculated high reflectivity of 67–72% confirmed the evident advantages of the Sc/Si multilayers. The performance of one Sc layer is so significant that even five periods are sufficient to give reflectivity of this order. In doing these calculations, we assumed that the boundaries between Sc and Si layers are perfectly sharp and smooth. This assumption is obviously not true for systems with intense diffusion and chemical reactions at interfaces. Therefore, to obtain the net conclusion about the practicability of Sc/Si coatings, these structures should be fabricated and tested.

A number of Sc/Si multilayers having a period $H = 18$–27 nm were prepared by DC-magnetron sputtering at 3×10^{-3} Torr of Ar. In addition, two Sc/Si coatings were deposited by electron beam evaporation of Sc and Si targets in vacuum chamber at a pressure 1.3×10^{-3} Pa. All multilayers were designed as having 10 periods, a protecting layer of Si on the top and a ratio of layer thickness $H(\mathrm{Sc})/H(\mathrm{Si}) = 0.786$. The sputtering rate was within the limits of 0.2–0.3 nm/s for Sc layers and 0.4–0.5 nm/s for Si layers. The deposition rates for electron beam evaporation were 0.25 nm/s for Sc and 0.11 nm/s for Si. The period and structure of fabricated multilayers were controlled by Cu K_α and Co K_α ($\lambda = 0.154$ and 0.179 nm) X-ray reflection at small and large angles as well as by cross-sectional electron microscopy. These measurements allowed to estimate the interface roughness as $\sigma = 1.3$ nm for the coatings fabricated by the magnetron sputtering and as $\sigma = 2.9$ nm for the mirrors prepared by the electron beam evaporation. The X-ray microanalysis of the Sc films showed that the electron beam evaporation gives a significantly higher content of oxygen in the Sc layers. The use of various substrates (floating glass, fused quartz and Si-wafers) had a minimal effect on the characteristics of the multilayers and their reflectivities.

Three methods were used to find the normal incidence reflectivity of fabricated concave Sc/Si mirrors: measurements with the soft X-ray/EUV reflectometer based on a laser-produced plasma source [9], measurements at BESSY synchrotron and measurements by using method [10] which is based on the comparison of the spectra of laser plasma source and the spectra of its image produced by the concave mirror under investigation. The results of these measurements and calculated characteristics of the mirrors are presented in Fig. 1 and Table 1. It is seen that results of reflectivity measurement carried out by different methods are in resonable agreement. The series of mirrors fabricated by the magnetron sputtering covers the whole interval under consideration and shows high reflectivity at all wavelengths. The reproducibility of results is within 3–5%, as one can judge, for example, from comparison of the optical parameters of the 2nd and 3rd, 7th and 8th mirrors presented in Table 1 which have very close periods. The highest reflectivity of 54% is achieved at $\lambda = 36.5$ nm, just near the threshold of excitations of the 3p-core electrons. Note that the measured reflectivities are about two times lower in comparison with the calculated ones, their maxima are shifted to shorter wavelengths by 1–4 nm and have widths which are narrower by 1–3 nm. These disagreements between theory and experiment are observed for all mirrors produced by magnetron sputtering and seem to be of a regular nature. They will be discussed later, after consideration of the microstructure of the coatings. Both mirrors fabricated by electron beam evaporation have low reflectivity (Table 1) as expected from their larger interface roughness and the higher content of oxygen in the Sc layers.

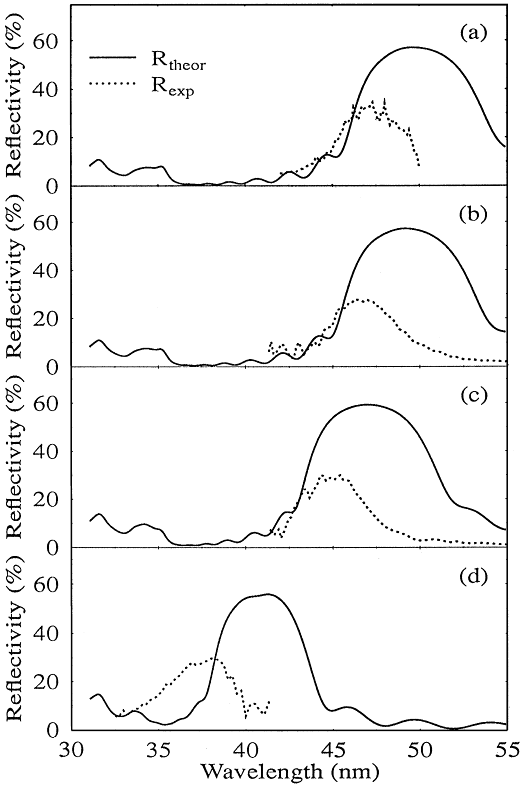

Fig. 1. Reflectivities of Sc/Si mirrors: (a) calculated (solid line) and measured by the reflectometer (dashed line) reflectivity of the multilayer with a period $H = 26.7$ nm at the incidence angle $\theta = 90°$; (b) calculated and measured by synchrotron radiation reflectivity of the multilayer with $H = 26.4$ nm at $\theta = 86°$; (c) calculated and measured by synchrotron radiation reflectivity of the multilayer with $H = 26.4$ nm at $\theta = 69°$ and (d) calculated and measured by synchrotron radiation reflectivity of the multilayer with $H = 19.5$ nm at $\theta = 86°$.

The electron microscopy study of multilayer cross-sections showed that the coatings prepared by the magnetron sputtering have smooth boundaries between Sc and Si layers with the evaluated roughness of 1.1 nm, while for the electron beam evaporation the roughness is of 3.5 nm. This agrees well with the estimations received from the small angle X-ray scattering in $\Theta/2\Theta$-geometry and with the observed reflectivity of the coatings. At the same time, all Sc/Si mirrors have regions of a mixed composition at both Sc–Si and Si–Sc interfaces. Adjacent to Sc are the two mixed regions about 6 nm thick for mirrors prepared by the magnetron

Table 1
Measured (calculated) optical characteristics of Sc/Si mirrors

Mirror	Period (nm)	Wavelength (nm)	Width (nm)	Reflectivity (%)
1	18.2	36.5 (38.5)	5.5 (5.8)	54 (71)
2	19.1	37.5 (39.6)	5.0 (5.9)	45 (71)
3	19.5	37.6 (39.9)	5.0 (6.2)	40 (71)
4	21.0	42.0 (42.0)	5.0 (6.5)	42 (72)
5	23.2	42.9 (44.5)	4.0 (7.0)	30 (70)
6	25.7	45.9 (47.6)	2.0 (7.6)	31 (67)
7	27.0	48.7 (49.1)	4.0 (7.9)	33 (67)
8	27.1	48.1 (49.2)	3.0 (7.9)	36 (67)
9	24.6	43.0 (44.5)	(7.0)	4 (71)
10	24.6	43.5 (44.5)	(7.0)	8 (71)

sputtering and about 8 nm thick for the electron beam evaporation. That is for the mirror with the period $H = 24.5$ nm these regions occupy from two-thirds to eight–ninth of the Sc layer depending on the preparation method. The rest of the layer is occupied by Sc grains with the grain size up to 3 nm (magnetron sputtering) or 5 nm (electron beam evaporation). Scandium in the grains has the FCC crystal structure with the lattice parameter $a = 0.465$–0.470 nm, instead of the HCP structure native for the bulk Sc.

Formation of the mixed regions is the result of diffusion of Si atoms into Sc layers during the deposition. The diffusion process is closely connected with the formation of the Sc_3Si_5 compound which is predicted by the binary Sc–Si phase diagram [11]. Both processes intensify with an increase in temperature. In particular, the heating of the multilayers up to 400°C is accompanied by a stronger intermixing of Si and Sc layers, vanishing of the Sc grains and a decrease in the period H. Electron diffraction shows the appearance of the Sc_3Si_5 compound in the Sc-based layer. Further heating up to 500°C enhances crystallization and recrystallization in Sc_3Si_5 layers with a transition to the interlayer coalescence. 1 h annealing at this temperature leads to a 12% decrease in the period, compared with the as-deposited state. Multilayers are destroyed completely if the annealing temperature rises above 500°C. These changes in the structure of the multilayers are accompanied by a rapid decrease in reflectivity. In particular, similar degradation takes place to some degree in coatings prepared by electron beam evaporation as this process occurs at temperature over 150°C. In a nutshell, we see that the diffusion and the formation of the Sc_3Si_5 compound leads to a very complicated structure of Sc-based layers which is essentially different from the ideal structure assumed in the calculations. The disagreement between experimental and theoretical results presented in Fig. 1 and Table 1 is mainly due to this difference in structure. It is very likely that the creation of diffusion barriers will result not only in sharper and smoother interfaces between Sc and Si layers, but also in coating reflectivity close to theoretical estimations.

In conclusion it may be said that the Sc–Si system was selected as a very promising material combination for coatings intended for the VUV interval of 35–50 nm. The key element of this combination is Sc. Its low absorption and high refractive indices which are evident from the trends in excitation of valence and 3p-core electrons make scandium a unique material for use at these wavelengths. Fabricated Sc/Si multilayers have the normal incidence reflectivity of up to 54%, which is close to the highest reflectivity of Mo/Si mirrors obtained at $\lambda = 13$ nm and is high enough for applications. Theoretical estimations as well as X-ray scattering and electron microscopy studies indicate that further progress in the preparation of sharper Sc–Si interfaces with lower roughness will probably result in a significant increase in reflectivity.

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