Subwavelength single layer absorption resonance antireflection coatings

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Abstract: We present theoretically derived design rules for an absorbing resonance antireflection coating for the spectral range of $100-400$ nm, applied here on top of a molybdenum-silicon multilayer mirror (Mo/Si MLM) as commonly used in extreme ultraviolet lithography. The design rules for optimal suppression are found to be strongly dependent on the thickness and optical constants of the coating. For wavelengths below $\lambda \sim 230$ nm, absorbing thin films can be used to generate an additional phase shift and complement the propagational phase shift, enabling full suppression already with film thicknesses far below the quarter-wave limit. Above $\lambda \sim 230$ nm, minimal absorption ($k < 0.2$) is necessary for low reflectance and the minimum required layer thickness increases with increasing wavelength slowly converging towards the quarter-wave limit.

As a proof of principle, $Si_xC_yN_z$ thin films were deposited that exhibit optical constants close to the design rules for suppression around 285 nm. The thin films were deposited by electron beam co-deposition of silicon and carbon, with N+ ion implantation during growth and analyzed with variable angle spectroscopic ellipsometry to characterize the optical constants. We report a reduction of reflectance at $\lambda = 285$ nm, from 58% to 0.3% for a Mo/Si MLM coated with a 20 nm thin film of $Si_{0.52}C_{0.16}N_{0.29}$.

OCIS codes: (310.1210) Antireflection coatings; (350.2460) Filters interference; (350.2450) Filters absorption; (050.5080) Phase shift; (050.6624) Subwavelength structures; (340.7480) X-rays, soft x-rays, extreme ultraviolet (EUV).

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1. Introduction

In optics, conventional antireflection coatings are often based on an asymmetric Fabry-Perot-like cavity which consists of a single dielectric layer of at least a quarter-wave thickness on top of a reflector. The interference effects in such a Fabry-Perot type resonator rely on the high transparancy of the non-absorbing dielectric medium, as the optical phaseshift is acquired over multiple passes within the cavity. Recently, multiple studies [1–5] have shown that antireflection resonance can also be achieved in highly absorbing thin films with a thickness far below the quarter-wave limit. These absorbing antireflection coatings (AARC) are ideally suitable for applications that, in addition to strong requirements of the reflectance, impose strict limitations on the thickness of the AARC.

In this paper, we consider, as an example of such an application, extreme ultraviolet lithography (EUVL) which operates by design at a wavelength of ~ 13.5 nm. Currently available sources of extreme ultraviolet (EUV) radiation are broadband [6, 7] and produce, in addition to EUV, radiation with comparable intensities in the spectral range of $100-400$ nm, defined here as deep ultraviolet radiation (DUV). The optical elements and photoresists [8] that are currently used in EUVL, are also equally sensitive to EUV and DUV radiation. As a consequence, the photoresist will be exposed to DUV radiation, which will reduce the contrast of the imprinted structure on the target wafer.

In previous work, van Herpen *et al.* [2] investigated the application of a single layer antireflection coating to the optical elements, in this case molybdenum silicon multilayer mirrors (Mo/Si MLM), to reduce their DUV reflectance. They showed that in order to maintain the EUV reflectance of the Mo/Si MLM, it is essential to maximize the optical transparency of the AARC for EUV radiation, by minimizing the thickness and using materials that are relatively transparent to EUV radiation. As a proof of principle they applied a 7 nm Si_3N_4 AARC on top of a Mo/Si MLM, which reduced the reflectance with a factor of 5 around $\lambda = 160$ nm.

In this paper, we rigorously derive design rules for an AARC, to be applied on a Mo/Si MLM, for the entire DUV range of 100 to 400 nm, in terms of optical constants and thickness. We show first experimental results on modifying the optical constants in the $250-400$ nm wavelength range, by varying the atomic concentrations in thin films of $Si_xC_yN_z$ to match the design rules for optical constants. Finally, we report on the realization of a $Si_xC_yN_z$ AARC on a Mo/Si MLM with an absolute reflectance of 0.3% at $\lambda = 285$ nm.

2. Theoretical optimization

The working principle of a single layer antireflection coating is based on the destructive interference between waves reflected off the two interfaces of the coating. For transparent materials, the phase shift, that leads to the destructive interference, is caused solely by the refractive property of the medium. For absorbing media, waves also gain a phase shift when reflected off an interface between two optically dissimilar media. By using an AARC, the non-trivial interface phase shift can complement the refractive phase shift, such that the minimum thickness constraint of $\lambda/(4n)$, applicable to transparent quarter-wave coatings, can be significantly lowered.

The reflectance calculations presented in this paper are based on the Abeles matrix formalism [9]. The multilayer mirror was defined as a periodic structure of 50 bilayers of molybdenum and amorphous silicon, on a semi-infinite crystalline silicon substrate. The bilayer thickness t was 7 nm and the fraction of molybdenum layer thickness with respect to the bilayer thickness was $\Gamma = t_{Mo}/t = 0.40$, which are typical values for a high reflectance ML for application. Optical constants for molybdenum, amorphous and crystalline silicon in the DUV range were taken from literature [10]. In the EUV range, optical constants for silicon and molybdenum were taken from Ref. [11] and Ref. [12] respectively, and optical constants for $\mathrm{Si}_x\mathrm{C}_y\mathrm{N}_z$ layers were computed from tabulated atomic scatter factors [13]. Under the assumption of perfectly sharp interfaces and a fixed angle of incidence of 1.5° with respect to the surface normal, only the thickness d and the complex index of refraction $\tilde{n} = n + ik$ of the AARC, with n the refractive index and k the extinction coefficient, enter as variables in the equations for calculating the reflectance in the DUV range.

3. Simulation results

A parameter space minimization of the reflectance $R(\lambda,d,n,k)$ for wavelengths in the DUV was carried out with respect to the thickness d and optical constants (n,k) of the AARC. We consider a reflectance below 10^{-3} to be acceptable for application and as such sets of AARC parameters (d,n,k), that satisfy the minimization criterion $R(\lambda,d,n,k) < 10^{-3}$, will be referred to as solutions. It is instructive to first show the typical behavior of $R(n,k)$ at two fixed thicknesses and wavelengths near the two opposite ends of the DUV wavelength range considered here. In Fig. 1, the reflectance as a function of n and k is calculated for $d = 2$ nm and $d = 25$ nm, for examplary wavelengths of $\lambda = 150$ nm and $\lambda = 350$ nm. Our calculations show that these four pictures are representative of the qualitative behavior of $R(n,k)$ for any wavelength in the DUV range. At small thicknesses the first minimum occurs at relatively large values for n. As the thickness increases, more local reflection minima appear and shift to lower values of n. The minimum thickness for which there first appears a local reflection minimum also increases with increasing wavelength. This can be seen in Fig. 1(c) where a thickness of 2 nm can not suppress the reflection of 350 nm radiation below 25%, regardless of the optical constants within the plotted range. It is not until for a thickness of approximately 25 nm that a reflectance below 10^{-3} can be achieved. Another recurring feature is, that at a fixed thickness and wavelength, the value of k at local reflection minima is larger for the minima that have a smaller value of n.

For the parameter space minimization, we limited the range of the parameters based on the following arguments. From an application point of view, the thickness should be minimized to in turn minimize EUV reflectance losses and therefore the range of d is given by $[d_{min}, d_{min} + 5\,\mathrm{nm}]$, where d_{min} is the smallest thickness for which the low reflectance requirement at that specific wavelength could be satisfied. Additionally, d_{min} was not allowed to be less than 2 nm, since the required refractive index will reach values exceeding $n = 10$, which are rarely encountered in materials. The optical constants n and k were allowed to vary in the range of $[0,10]$ and $[0,5]$ respectively. Values outside these ranges are highly uncommon for any material.

In Fig. 2(a) the colored area shows the range of values of AARC thickness d, for which there exists a set of optical constants (n, k) within the allowed range, for which $R < 10^{-3}$. The corresponding range of values for n and k is plotted in Figs. 2(b) and Figs. 2(c), respectively.

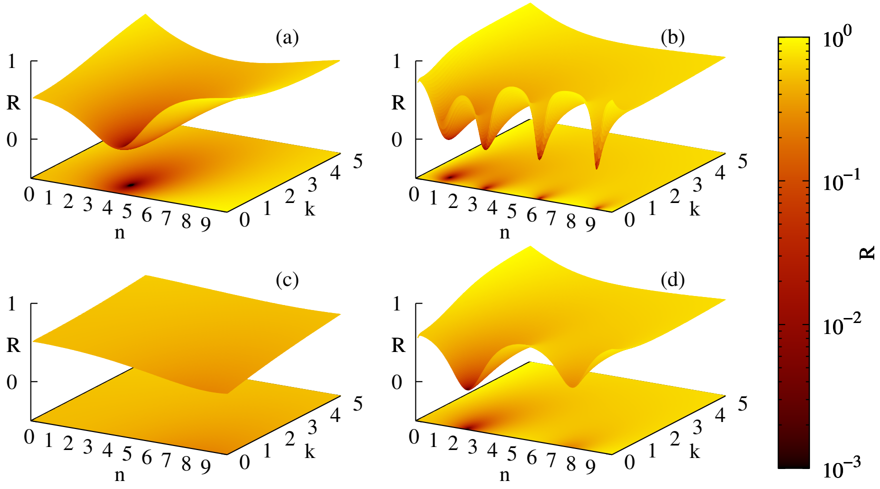

Fig. 1. Examples of calculated reflectance for a Mo/Si MLM coated with a single layer AARC with thickness (a,c) $d = 2$ nm and (b,d) $d = 25$ nm, as a function of the refractive index n and extinction coefficient k of the AARC, for (a,b) $\lambda = 150$ nm and (c,d) $\lambda = 350$ nm. The contour surface in the nk-plane is a projection of the three-dimensional reflectance surface onto the nk-plane. The vertical axis of the threedimensional surfaces represents the reflectance on a linear scale, whereas the colour map represents the reflectance on a logarithmic scale.

The apparent upper limit in Fig. 2(a) is just a result of the parameter restriction $d < d_{min} + 5\,\text{nm}$. If the maximum thickness is not constrained, a lot more solutions can be found, but due to the requirement of AARC thickness minimization, these solutions are not of interest. When considering Fig. 2, there appears to be a distinct wavelength that divides the graphs into two wavelength regimes. Below 227 nm the lower limit in layer thickness d, results from the imposed parameter range constraints (i.e. $d > 2$ nm) as described before. The existence of solutions with $R(d,n,k) < 10^{-3}$ at these low values for d, demonstrates that a single AARC with a thickness of only 2 nm, given the appropriate complex index of refraction, already could provide full suppression of reflectance for any wavelength in the range $100-227$ nm. In strong contrast, for $\lambda > 227$ nm, the minimum required thickness for near-zero reflectance increases with increasing wavelength. In this case, this lower limit is not due to parameter constraints, but rather because no solutions $R(d,n,k) < 10^{-3}$ exist in that parameter range.

The division into two wavelength ranges that is apparent in Fig. 2(a) can also be observed in Figs. 2(b) and Figs. 2(c). Below 227 nm, the refractive index n is monotonously increasing. The propagational phase shift is proportional to $(nd)/\lambda$, so for increasing wavelength and constant thickness, in order to maintain the required phase shift for destructive interference, the refractive index needs to increase. Above 227 nm, a further increase in n would result in a too high reflected amplitude at the top interface that can no longer be compensated by the wave reflected off the bottom interface. For this reason, above 227 nm the conditions for a low reflectance can only be obtained by increasing the AARC thickness. In addition, above 227 nm the absorption k has to be reduced or the wave traversing the AARC will be absorbed too heavily and will not be able to fully cancel out with the wave reflected off the top interface by destructive interference.

An important observation can be made from Fig. 2: consider the red line drawn in Fig. 2(a), which designates the minimum thickness, for which it is still possible to achieve high suppres-

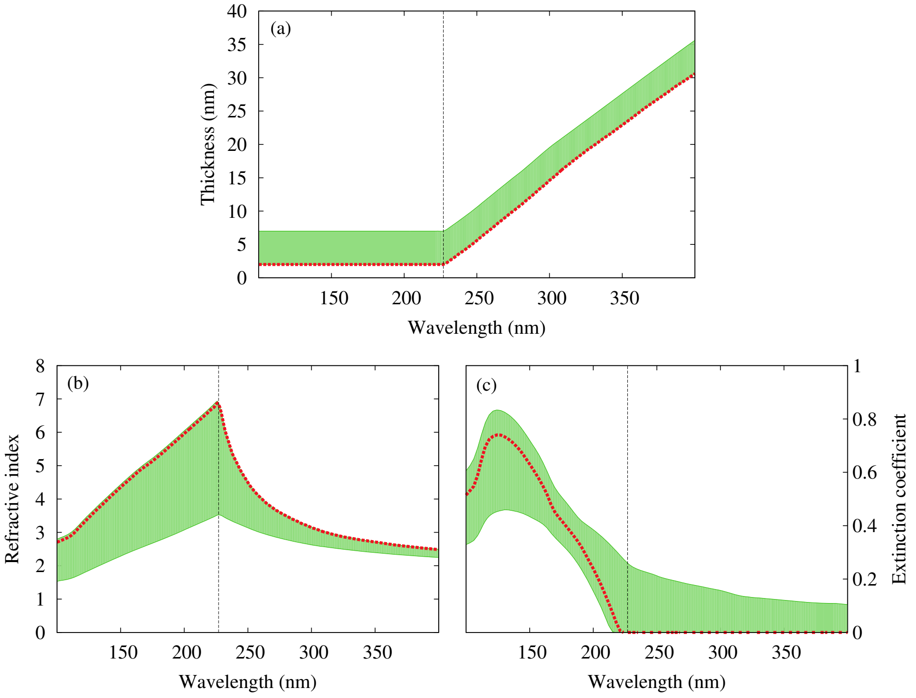

Fig. 2. The range of AARC parameters, (a) thickness, (b) refractive index and (c) extinction coefficient for which a solution of $R(\lambda,d,n,k) < 10^{-3}$ is found. In (a) the red dashed line indicates the minimum thickness at each wavelength for which the reflectance constraint can be satisfied. The corresponding values for n and k are indicated by the same dashed red line in (b) and (c), respectively. The vertical black dotted-dashed line marks the division of the two wavelength ranges as discussed in detail in the text.

sion of DUV. For these particular thicknesses there are corresponing values of n and k for the condition of minimum reflection, indicated by the red lines in Figs. 2(b) and Figs. 2(c), respectively. These curves state that if we were to equip the model Mo/Si MLM with a 2 nm thin film that exactly possesses the plotted (n, k) dependency, the reflectance would be less than one promille for every wavelength in the range $100-227$ nm. This shows that a single AARC is not fundamentally limited to operate centered around a single wavelength but can, with the appropriate optical constants, fully suppress a large range of wavelengths. It is important to note that not every arbitrary curve of optical constants can be achieved in practice, due to practical limitations and the fundamental relation between the real and imaginary part of the optical constants given by the Kramers-Kronig relation. Additionally, even if the required optical constants are theoretically allowed, producing a material with these properties is far from a trivial matter. Still, these simulations show that appropriately modifying the optical constants of thin film AARC's in a specific wavelength range could strongly improve the antireflective efficiency.

Returning to the first proof of principle by van Herpen [2], which showed that an AARC of 7 nm of Si_3N_4 suppressed the reflectance of 160 nm radiation of a Mo/Si MLM by a factor of 5 at a loss of 4.5% absolute EUV reflectance, our results demonstrate that theoretically there is much room for improvement. With the appropriate optical constants, the DUV reflectance could be further reduced to below 10^{-3} using an even thinner AARC, which will further reduce the losses in EUV reflectance, assuming the optical constants of the AARC in the EUV remain identical. A larger challenge is found in the design and manufacturing of antireflection coatings for the wavelength range above 227 nm. In this case, the steadily increasing thickness and decreased range of viable extinction coefficients, decrease the range of refractive indices that allow for efficient suppression of DUV reflectance, requiring a higher accuracy in reproducing these optical constants.

In the DUV range, optical constants are not just dependent on atomic composition and material density, but are also dependent on local structure and chemistry. Therefore, there exists no simple formalism to predict the DUV optical constants of an arbitrary material, based on only the material's density and atomic composition. The development of materials, that meet the requirements for application as AARC in the DUV, relies on experimental optimization. As a first experimental demonstration of the above principles, we report the fabrication of a material that possesses the required optical constants to suppress reflectance centered around 285 nm.

4. Experimental

We deposited B_xSi_y, B_xC_y, Si_xC_y and $Si_xC_yN_z$ thin films with thicknesses between $10-20$ nm onto the native oxide of single crystalline silicon substrates. The films were deposited in a UHV chamber with base pressure of 10^{-8} mbar using simultaneous electronbeam evaporation of silicon, boron and carbon. For the $Si_xC_yN_z$ films, a Kaufman type hot cathode ion source was used for nitrogen-ion production, with an ion energy of 100 V and an ion flux of $\sim 10^{14}$ cm^{-2}. The atomic ratios were controlled by varying the relative deposition speeds of silicon, boron and carbon with respect to the constant supply of nitrogen. The resulting film stoichiometry was determined in vacuo using X-ray photoelectron spectroscopy. We selected silicon-, boron- and carbon-based materials for investigation, because their optical constants in the DUV, as found in literature [10], approximated the required optical constants as calculated in the previous section and they are relatively transparent to EUV radiation. We performed grazing incidence X-ray reflectivity measurements to construct a structural model for the deposited thin films in terms of film thickness, density and substrate/top interface roughnesses. The structural model served as a basis to model the complex index of refraction of the thin film by fitting the polarization-dependent reflection spectra from variable-angle spectroscopic ellipsometry measurements.

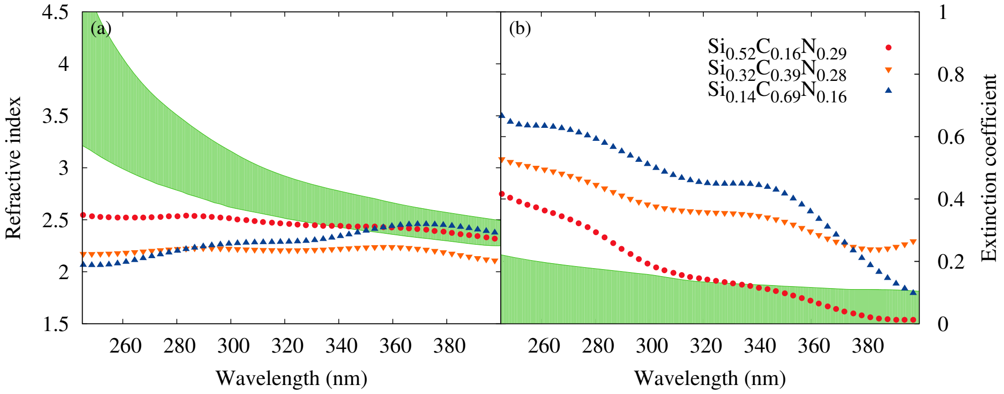

Fig. 3. Optical constants for three SiCN thin films with varying stoichiometry obtained by variable angle spectroscopic ellipsometry. (a) The refractive index. (b) The extinction coefficient. The green colored areas in panel (a) and (b) correspond to the colored areas in Figs. 2(b) and Figs. 2(c) respectively

In Fig. 3, the optical constants of three SiCN films are shown, representative for a more extensive series of $Si_xC_yN_z$ samples that was produced. Both the refractive indices and the

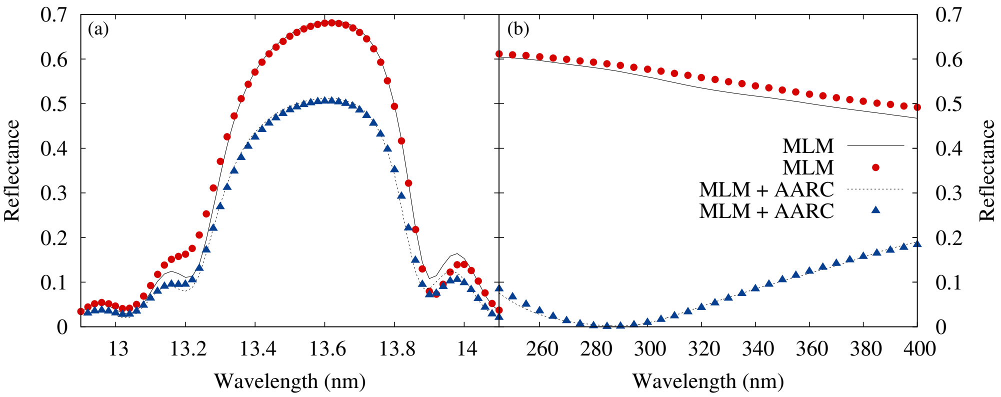

Fig. 4. Calculated (solid lines) and measured (symbols) EUV (a) and DUV (b) reflectance of a Mo/Si MLM without (red markers) and with a 20 nm film of $Si_{0.52}C_{0.16}N_{0.29}$ on top (blue markers).

extinction coefficients show comparable values to the calculated optical constants required for application as AARC, indicated by the green area, but barely overlap. It is important to note that a mismatch in refractive index can be compensated by increasing the thickness of the AARC to obtain sufficiently low reflectance. However an extinction coefficient that is too large can not be compensated. The refractive indices of the B_xSi_y, B_xC_y, Si_xC_y thin films, had comparable values to the refractive indices of the $Si_xC_yN_z$ samples (see Fig. 3(a)), but the extinction coefficients had values between $1-3$, which is significantly larger compared to the extinction coefficients of $Si_xC_yN_z$ (see Fig. 3(b)) and the calculated range of optimal extinction coefficients. From the materials we have evaluated, SiCN was the most promising candidate to be applied as AARC on Mo/Si MLM's for DUV suppression.

As a proof of principle, we coated a Mo/Si MLM with a thin film of $Si_{0.52}C_{0.16}N_{0.29}$ with a thickness of 20 nm, which calculations have shown to be optimal for maximal suppression of 285 nm. The DUV and EUV reflectances were measured at the Physikalisch Technische Bundesanstalt (PTB) at the Berliner Electronenspeicherring-Gesellschaft für Synchrotronstrahlung storage ring in Berlin. The measured and calculated reflectances for the uncoated and AARC coated MLM, in the EUV and DUV, are shown in Fig. 4. The theoretical and experimental data agree quite well and the slight discrepancies can be explained by slight differences in optical constants used for molybdenum and silicon in calculations with respect to the true optical constants of the thin films in the mulitlayer mirror. We observe a broadband suppression in the $250-400$ nm wavelength range, centered around 285 nm and absolute reflectance at $\lambda = 285$ nm is reduced from 58% to 0.3%. The EUV reflectance is reduced from 68%, for the uncoated mirror, to 50% for the mirror capped with the SiCN antireflection coating.

It should be noted that the optical constants for $Si_{0.52}C_{0.16}N_{0.29}$ deviate from the calculated optimum values (see Fig. 2). As a result the AARC thickness of 20 nm used for the application is much larger than the minimum thickness of 11.8 nm, that could have been used given optimal optical constants. Further experimental optimization, to reproduce the optimal DUV optical constants more accurately, would allow for a thinner AARC and subsequently smaller EUV losses. Finally, the minimization of EUV reflectance losses was only considered in the selection of transparent materials for this experimental pilot study but was not included in the theoretical optimization of DUV optical constants presented in this work. A more extensive combined EUV/DUV optimization of optical constants should be performed to maximize DUV suppression with respect to EUV loss.

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