High performance EUV multilayer structures insensitive to capping layer optical parameters

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Abstract: We have designed and tested a-periodic multilayer structures containing protective capping layers in order to obtain improved stability with respect to any possible changes of the capping layer optical properties (due to oxidation and contamination, for example)-while simultaneously maximizing the EUV reflection efficiency for specific applications, and in particular for EUV lithography. Such coatings may be particularly useful in EUV lithographic apparatus, because they provide both high integrated photon flux and higher stability to the harsh operating environment, which can affect seriously the performance of the multilayer-coated projector system optics. In this work, an evolutive algorithm has been developed in order to design these a-periodic structures, which have been proven to have also the property of stable performance with respect to random layer thickness errors that might occur during coating deposition. Prototypes have been fabricated, and tested with EUV and X-ray reflectometry, and secondary electron spectroscopy. The experimental results clearly show improved performance of our new a-periodic coatings design compared with standard periodic multilayer structures.

OCIS codes: (310.4165) Multilayer design; (340.7480) X-rays, soft x-rays, extreme ultraviolet (EUV); (220.3740) Lithography.

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1. Introduction

The reflectance of EUV multilayer (ML) structures can be degraded significantly by hydrocarbon contamination or by the growth of an oxide layer on the top surface due to environmental contaminants present in the operating environment. Carbon contamination has been analyzed by J. Hollensheada and L. Klebanoff [1], who show that it originates from radiation-induced direct dissociation of carbon composite molecules. Contamination by heavier hydrocarbons is most problematic, as light hydrocarbons can be removed by heating the optics up to about 30°C. Oxidation of multilayers in a photo-lithographic apparatus, which can be in fact a much more serious problem, is mainly due to the presence of water vapor in the residual gas. The oxidation depends on the interaction between EUV photons and the multilayer material: EUV photons cause primary electron emission by the photoelectric effect and the primary electrons in turn generate secondary electrons by interaction with the atoms of the multilayer materials. The mean free path of secondary electrons in the materials is only a few nanometers, so only those electrons generated in the top few layers [2-4] can reach the vacuum. Free radicals created by secondary electrons having sufficient energy can bond to the capping layer atoms and form oxides on the surface, or diffuse into or through the top layer and cause oxidation.

To overcome the problem of surface contamination and oxidation, the use of protective capping layers such as Ru has been investigated [4-6]. An extensive analysis of the critical parameters affecting the EUV-induced damage of Ru capping layer has been performed by Hill et al. [6]. However a capping layer deposited on an optimized periodic structure will significantly reduce the reflectivity of the coating. Even a reflectivity reduction of only 1% can result in an overall 18% reduction for a ten element optical system, such as those now being developed for EUV lithography.

In this work we analyze performance and stability properties of an innovative multilayer coating design capable to provide higher efficiency in a lithographic apparatus [7]. These structures, which deviate from conventional periodic multilayer design, represent also a solution to the multilayer surface stability problem.

A-periodic multilayers having performance tailored to specific applications, e.g, wide spectral bandwidth to reflect ultrashort pulses, wide angular bandwidth, high peak reflectivity, etc., have been investigated previously [8-16]. The a-periodic multilayer structures we have developed are designed using a new optimization procedure based on the maximization of a merit function which takes into account the lithographic source spectrum and the number of mirrors in the apparatus. The algorithm optimization is based on evolutive strategy that guarantees solutions that are stable even to random errors in the layer thicknesses that might

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occur during multilayer deposition. As we describe below, these capped a-periodic multilayer coatings offer several advantages that will yield significant performance improvements, for EUV lithography and potentially for other applications as well.

2. Design procedure

When EUV radiation interacts with a multilayer structure, the superposition of the incident and reflected electromagnetic waves generates a standing wave field distribution in the multilayer stack, as illustrated in Fig.1.

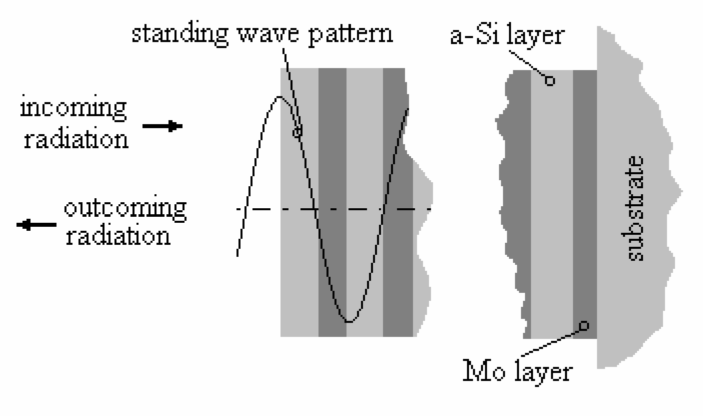

Fig.1. Schematic representation of the standing wave into a multilayer structure

By regulating the distribution of the standing-wave field inside the structure (i.e. by modifying the thickness of each or of some particular layers) it is possible to control some specific properties of the ML.

The structures presented are based on an a-periodic design. The a-periodicity allows for a better spectral match of the emission distribution of the lithographic source (i.e. the stationary wave field is distributed to maximize interference of reflected components by considering multi-reflection inside each layer), thereby increasing the flux that ultimately reaches the image plane of the optical system; these coatings are significantly less sensitive to layer thickness errors that might occur during deposition, so their actual optical performance is closer to the theoretical value. Moreover the applied optimization process takes into account interface roughness and intermixing, thus producing designs which can be more faithfully realized in practice.

Moreover in these structures the thickness of the last top layers allows to spatially shift the capping layer position with respect to the position of the standing-wave anti-node at the top of the multilayer, i.e., at the working wavelength, the standing-wave field strength can be minimized in the capping layer. In this way the energy absorbed in the top layer is reduced, thus allowing more layers to contribute to the reflected wave intensity. Our simulations show that: a) the reflectance of these structures is much less sensitive to capping layer oxidation, thus the coatings will be more resilient in an environment with a relatively high oxygen concentration; b) they are significantly less sensitive to the capping layer materials optical properties, thus allowing for a much wider choice of capping layer materials, and much less sensitivity to hydrocarbon contamination. Properties a) and b) could be obtained in principle also with standard periodic multilayer, in which the thickness of the last top layers is adjusted in order to suitably shift the standing wave, sacrificing the best performance in terms of spectral match of the lithographic source (and therefore of integrated total flux) and stability with respect to layer thickness errors.

Considering that ML reflectivity $R(\lambda)$ depends very critically on the parameters of the layer stack, i.e., layer thicknesses and interface widths , an “evolutive strategy”[1] has been used in the optimization procedure. The evolutive approach differs from a local optimization

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algorithm [14] that would explore only a limited domain region, and from typical global optimizations such as genetic algorithms [13], which would be too weak to focus towards a domain region with overconfidence. The procedure we have adopted has in addition the important property of converging to stable solutions, i.e. those not affected by relatively small changes in ML parameters [7,8]. Thus the optimization procedure developed here uses an algorithm able to acquire domain knowledge based on the merit function values obtained during the optimization process. Interfacial roughness and/or interdiffusion values at the interfaces are also taken into account. The specific merit function we used to maximize the reflected EUV flux is $\int R(\lambda)^M * I(\lambda)d\lambda$, where $I(\lambda)$ is the source spectrum, $R(\lambda)$ is the reflectivity of the structure, and M is number of mirrors in the apparatus; in this work we have assumed M=10, and a Sn laser-produced plasma source has been assumed. (Comparable coatings could also be developed for other sources as well.) In Fig. 2 we show the typical spectrum emitted by a Sn laser plasma, see for example [17] .

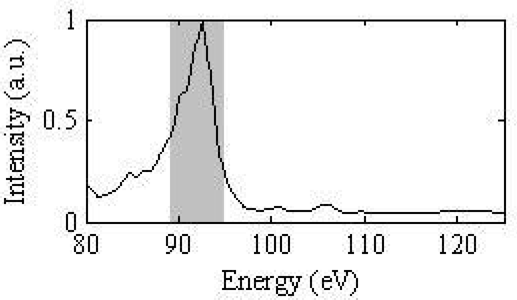

Fig. 2. The typical spectrum emitted by a tin laser plasma, the shadowed area corresponds to the spectral components utilized by multilayer optics for the EUV lithography.

3. Experiment: samples design, reflectivity and secondary electron measurements

In order to experimentally test the improved performance expected from our simulations, prototype Mo-Si multilayer structures, both standard periodic and aperiodic, have been designed, fabricated and tested. In Fig. 3 the structure of a-periodic design is reported. The periodic multilayers have been designed without modifying the last a-Si layer thickness in order to experimentally test the properties deriving from the standing wave shift.

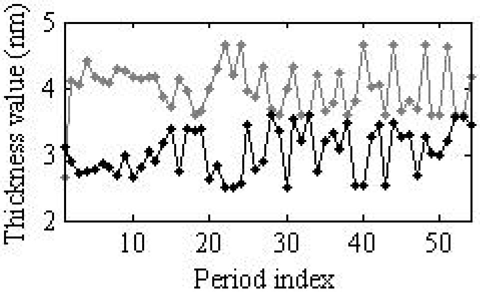

Fig. 3. A-periodic structure layers thickness: in gray a-Si, in black Mo. The abscissa represents the increasing period number starting from the most external to the internal layer.

In the design optimization procedure a RuO_2/Mo capping layer, in order to take into account the oxidation of the Ru uppermost layer, and an interface width of 0.5 nm have been assumed. Accordingly the optimization algorithm searched for solutions among those less sensitive to the radiation absorption in the capping layer. In addition to the Ru-capped multilayers just described, we also simulated the performances of the multilayer structure capped with Pt and a-Si as well. In the latter case the a-Si uppermost layer was allowed to form a 1 nm thick oxide layer. In Fig. 4 the results of our simulations are reported:

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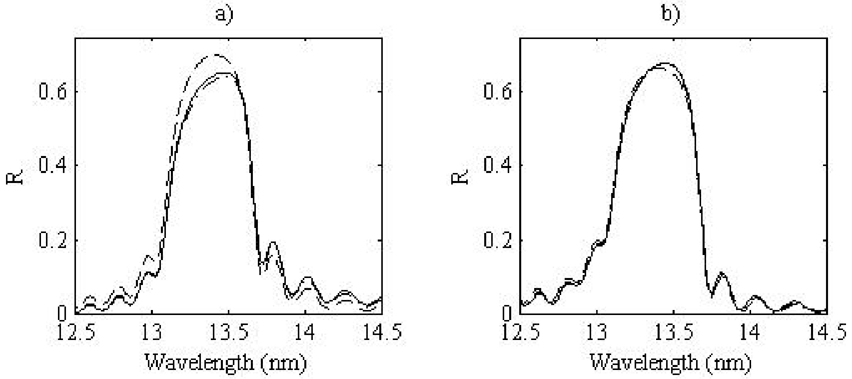

Fig. 4. Theoretical calculations of the reflectivity curves: case a) standard periodic ML, case b) a-periodic chaotic ML; in both cases: continuous line, MLs with Ru/Mo capping layer; dash dotted line, ML with Pt/Mo capping layer; and dashed line, ML with a-Si/Mo capping layer.

while the a-periodic structure shows higher reflectivity than the periodic structure in the case of multilayers containing Pt and Ru capping layers, the opposite is true for samples containing a-Si capping layers. (Unfortunately it is generally recognized that an a-Si capping layer is not a suitable solution for a photolithographic apparatus, due to poor resilience to oxidation.) Furthermore, by comparing the simulated performance of the different periodic and a-periodic structures, we find that the new structures presenting suitable shift of the standing wave node, both periodic, with last Si layer optimized [5], or a-periodic, are less sensitive to the choice of capping layer while in the case of periodic structures of standard design a strongly absorbing capping layer causes a significant reduction of reflectivity.

Prototype Mo/Si multilayers were deposited by magnetron sputtering in Reflective X-ray Optics' (RXO) "S-Gun" deposition system [18]. Multilayer structures containing 50 periods tuned near 13.5 nm were deposited onto 3" Si (100) wafers. Both periodic and aperiodic coatings were produced, with either 4.05nm/2nm Si/Mo, 2.0 nm/2.0nm Ru/Mo, or 1.0 nm/2.0 nm Pt/Mo capping layers. As already said the periodic structures do not provide any standing wave node shift and have been used to prove the noticeable effect deriving from suitable shift of the standing wave to put its node coincident with the capping layer.

Samples were tested through EUV and X-ray reflectivity measurements as well as with secondary electron yield measurements. EUV reflectance was measured immediately after deposition and then again a few months later when secondary electron yield measurements were performed. The EUV reflectance was measured after deposition as a function of wavelength from 12.5 to 14.5 nm in RXO's laser-plasma reflectometer[18].

In Fig. 5 the experimental reflectivity curves for periodic and aperiodic Mo/Si structures having a-Si/Mo, Ru/Mo, and Pt/Mo capping layers are shown. The peak reflectivity values are listed in Table 1. Note that because the deposition rates drift slightly over time in this particular deposition system, the multilayers do not all peak at the exact same wavelength; however the various reflectance curves in Fig. 5 have been slightly shifted in wavelength to facilitate comparison. Note also that the peak reflectance measured in the laser-plasma reflectometer has been verified to be systematically lower by about ~2% absolute compared with measurements made using synchrotron radiation at the ALS facility in Berkeley.

The experimental results shown in Fig. 5 are consistent with the theoretical simulations: a-periodic multilayer structures have better performance than the periodic structures in the case of Ru/Mo and Pt/Mo capping layers. Due to the high transparency of a-Si at this wavelength, however, the situation for the case of the aperiodic Mo/Si multilayer with a-Si as capping layer shows different behavior: here the periodic structure gives the best reflectivity.

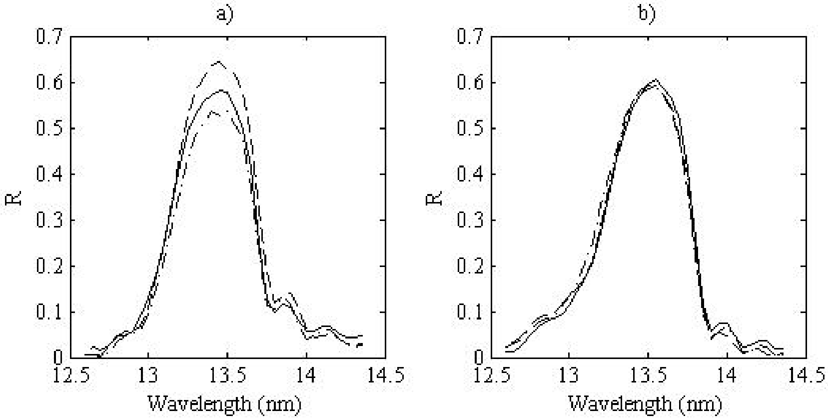

Fig. 5. Experimental reflectivity curves: case a) standard periodic ML, case b) a-periodic chaotic ML; in both cases: continuous line, MLs with Ru/Mo capping layer; dash dotted line, ML with Pt/Mo capping layer; and dashed line, ML with a-Si/Mo capping layer.

Table 1. Peak reflectance values for the six samples: italic, values measured at RXOLLC and underlined, values measured at ELETTRA.

	ELETTRA *RXO*	ELETTRA *RXO*
	Periodic	A-periodic
Ru/Mo	0.5634 *0.5820*	0.6125 *0.6051*
Pt/Mo	0.5495 *0.5372*	0.5984 *0.5926*
a-Si/Mo	------- *0.6445*	------- *0.5910*

On the other hand, as discussed above, a-Si protective capping layers are not suitable for photolithographic applications due to poor resistance to oxidation [19].

The X-ray reflectance (XRR) of our prototype samples was measured from 0 to 6 deg (grazing angle) using Cu Ka (1.54Å) radiation. The XRR curves are reported in Fig. 6 for periodic, Fig. 6(a), and aperiodic, Fig. 6(b), structures with Ru capping layers. Both the experimental XRR curves and the fits are reported. Similar data have been obtained for the other samples listed above as well. The XRR data show clearly Bragg peaks up to the 9th order for the periodic case, while in the aperiodic case the peak amplitude rapidly decreases for the higher orders, and so peaks only up to the 5th order can be clearly distinguished from the noise. The XRR period was adjusted in the calculations to match the measured data for the periodic structures: the periods were thus found, respectively in the cases of Si, Ru and Pt capping layers, to be 7.05 nm , 6.985 nm, and 6.875 nm. (The decrease in period is the result of the drift in deposition rate characteristic of the deposition system mentioned above.) In the case of the aperiodic multilayers, no fitting was performed: the calculations shown were computed using the nominal design parameters. The good agreement between measurements and calculations confirms that the actual layer thicknesses deposited are reasonably close to the design layer thicknesses in all cases.

From the measured reflectivity curves (Fig. 5) it is clear that the aperiodic structures show a behavior substantially insensitive to the capping layer material while in the case of periodic structures the reflectivity curves show a significant decrease of the peak with the different capping layer materials, Pt, being the most highly absorbing material, giving the worst performance.

Several months (6 months) after the coatings were deposited, reflectivity measurements and secondary electron emission measurements were performed at the bending magnet BEAR beam line of the ELETTRA synchrotron (Trieste - Italy) on samples containing Ru and Pt capping layers. The primary electrons emitted via the photoelectric effect by monochromatic photons in an energy interval around the multilayer working wavelength generate secondary electron emission. These secondary electrons have a mean free path of only a few nm so the measured signal originates from a very thin layer below the top surface of the multilayer structure. Consequently the secondary electron signal can be related to the amplitude of the standing wave field resulting from the superposition of the incident and reflected waves at the top surface of the multilayer structure.

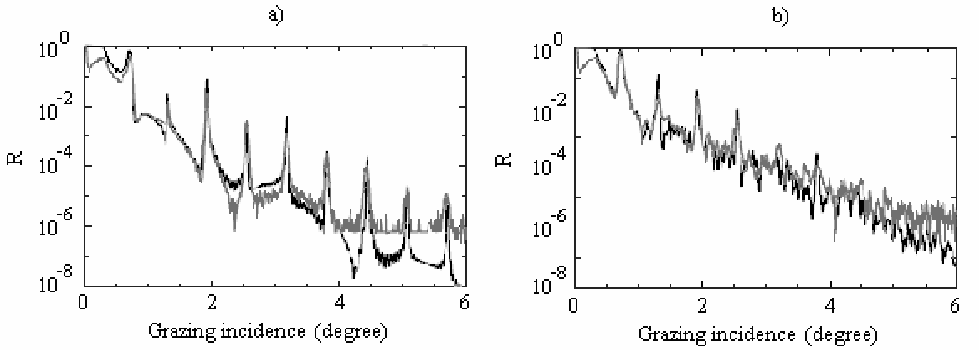

Fig. 6. X-ray reflectance (XRR) measured from 0 to 6 deg (grazing) using Cu Kα (1.54Å) radiation. The structures considered are periodic (case (a)) and a-periodic (case (b)) over-coated by Ru/Mo capping layer. In both cases in gray the measured data and in black the fitting result.

The reflectivity of periodic and a-periodic samples having Pt and Ru capping layers have been measured in both s and p polarization. In Fig. 7 the reflectivity curves for 10° incidence angle, average polarization and in the energy interval between 85 and 100 eV are reported.

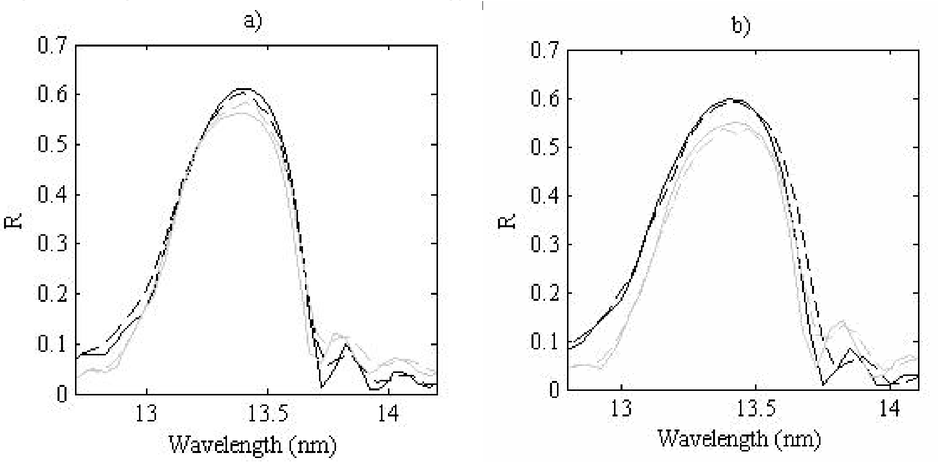

Fig. 7. Experimental reflectivity curves measured at ELETTRA and RXO. In the case (a) a-periodic and periodic structures with Ru/Mo capping layer, in the case (b) a-periodic and periodic structures with Pt/Mo capping layer; in both cases: continuous black line, a-periodic structure measured at ELETTRA; dashed black line, a-periodic structure measured at RXO; continuous gray line, periodic structure measured at ELETTRA; and dashed gray line, periodic structure measured at RXO.

For comparison the curves previously measured at RXO are shown as well. In order to correctly compare these data, we must take into consideration that the peak reflectivity values measured at RXO using a laser-plasma reflectometer are slightly lower than the values

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measured using synchrotron radiation at the ALS, so we expect to find the same behavior for the ELETTRA data, see also Table 1. It is clear that the two a-periodic samples show essentially the same peak reflectivities as measured immediately after deposition. These data confirm the superior performance of the coatings with standing wave shift. Furthermore, the periodic samples show further reduction of the reflectivity compared with the values obtained just after deposition, and in particular this decrease is greater for the Ru-capped coatings than for Pt–capped coatings. This fact could be ascribed to Ru oxide formation at the top surface, as Pt is known to be more chemically stable.

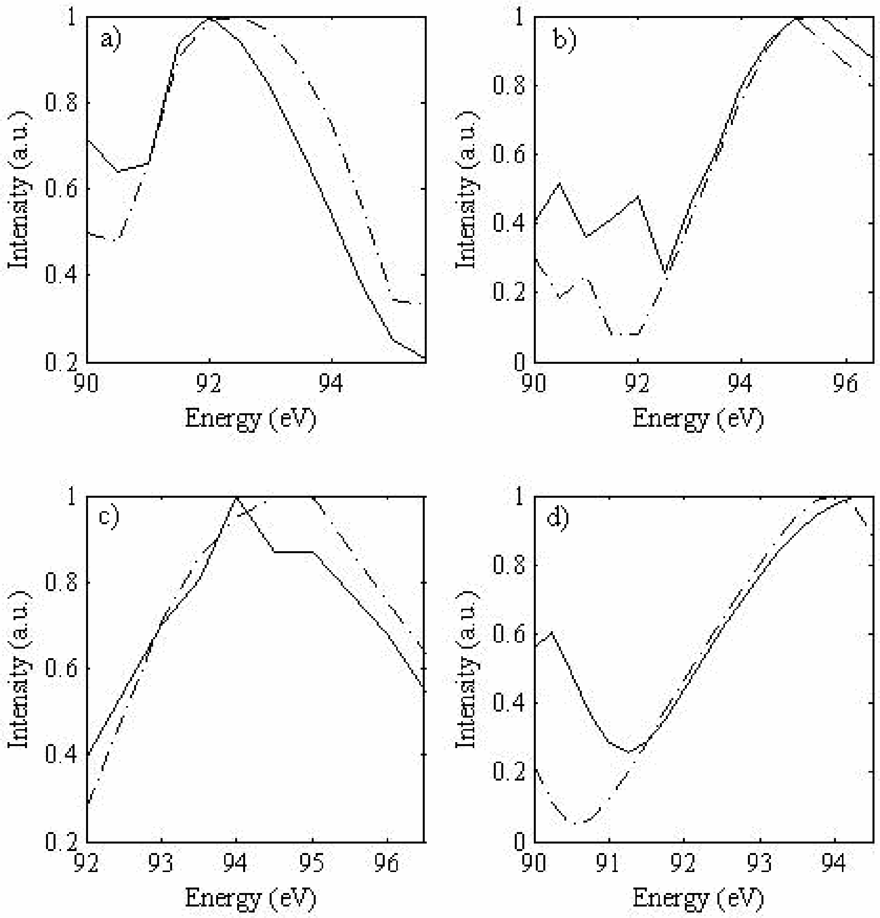

Fig. 8. Experimental (continuous line) results of photoemission compared with theoretical (dash dotted line) prediction of the standing wave intensity in the top of the ML, see text. In sub section (a) the periodic case over capped by ruthenium, in sub section (b) the a-periodic case over capped by ruthenium, in sub section (c) the periodic case over capped by platinum and in sub section d) the a-periodic case over capped by platinum.

Photoemission measurements were performed only in s polarization, as theoretical evaluations showed that the standing wave field distribution in the uppermost layers of the structure was essentially independent on the polarization state of the radiation. The electron analyzer was set at 45° from the normal to the sample surface in order to have the best performance. The sample was positively biased at 20 V thus giving more kinetic energy to the escaping electrons, and consequently nearly saturating the detector, and allowing us to set

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the analyzer electron energy window to begin at 20 eV. Photoelectron detection at the exit of the analyzer was measured using a microchannel plate. The energy of the impinging radiation beam was scanned through the peak of the measured reflectivity curve of each ML while the angle of incidence was maintained at 10°.

The normalized, integrated signal of secondary electrons (SEY), from 20 to 50 eV is shown versus the scanning radiation energy in Fig. 8 for both periodic and aperiodic samples. In the same figure, for comparison, we show the calculated standing wave field intensity integrated below the vacuum interface of the ML. In order to take into account the mean free path, L, of secondary electrons in the materials, the intensity, I(z), versus the depth from top of the ML structure has been weighed according to the formula $I(z)\cdot e^{-(z/L)}$ [1]. L is about 1 nm for the materials considered. The ML parameters derived from the XRR measurements were used in the case of periodic structures, while for the a-periodic structures a constant correction to each layer was applied in order to properly match the measured reflectivity curves. In particular, the thickness of each layer was reduced by 0.35 Å in the case of Ru capped structures, while the thickness of each layer was increased by 0.15 Å for the Pt capped structure. The good correspondence between the theoretical and experimental curves confirms that the signals correspond to the standing wave distribution in the ML.

Finally we compare the SEY at the photon energy corresponding to the reflectivity peak for each multilayer studied. In Table 2 we list the ratio between the SEY values measured for the various samples. The SEY ratio between aperiodic and periodic ML structures having Pt capping layers is 0.022, while the ratio for structures having Ru capping layers is 0.54,. The SEY ratio between aperiodic structures having Pt and Ru capping layers is 0.057, while the SEY ratio for periodic structures is 1.42. These measurements have random errors of the order of a few percent. As secondary electrons can promote oxidation [4], the SEY data presented in Table 2 therefore further suggest that the a-periodic structures, or structures with minimum of standing wave at the cap-layer position, will be more resilient to oxidation, with a-periodic Pt-capped samples likely having greater resilience relative to Ru-capped coatings. It should be noted that Pt has not been considered for use as a capping layer material for EUVL coatings until now, because of its strong absorption at 13.5 nm; however our results suggest improved performance of Pt-capped multilayers relative to Ru-capped multilayers.

Table 2. The ratio between the total secondary electron yield signals taken at the reflectivity peak.

(A-periodic Ru/Mo)/(Periodic Ru/Mo)	54 %
(A-periodic Pt/Mo)/(Periodic Pt/Mo)	2.2 %
(A-periodic Pt/Mo)/(A-periodic Ru/Mo)	5.7%
(Periodic Pt/Mo)/(Periodic Ru/Mo)	142 %

4. Conclusion

EUV ML structures have been designed using a new optimization scheme based on an evolutive strategy. The ML structures have been optimized in order to achieve the highest possible reflectivity at 13.5 nm while simultaneously yielding low sensitivity to capping layer optical properties. We have fabricated and tested prototype samples of these structures, made of Mo/a-Si bilayers with Ru, Pt and a-Si capping layers. EUV reflectance measurements were performed after deposition using a laser-plasma reflectometer, and also 6 months later using synchrotron radiation. XRR and secondary electron yield measurements have been made as well. Our experimental results demonstrate the superior performance of capped, a-periodic structures compared with conventional periodic coatings, showing higher reflectivity, lower secondary electron emission, better stability over time, and insensitivity to the choice of capping layer material. We propose that these structures can be used for EUV lithography applications in order to realize significant performance enhancements.

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