Interface engineered ultrashort period Cr–Ti multilayers as high reflectance mirrors and polarizers for soft x rays of \( \lambda = 2.74 \) nm wavelength

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Cr–Ti multilayers with ultrashort periods of 1.39–2.04 nm have been grown for the first time as highly reflective, soft-x-ray multilayer, near-normal incidence mirrors for transition radiation and Čerenkov radiation x-ray sources based on the Ti–2\( p \) absorption edge at \( E = 452 \) eV (\( \lambda = 2.74 \) nm). Hard, as well as soft, x-ray reflectivity and transmission electron microscopy were used to characterize the nanostructure of the mirrors. To achieve minimal accumulated roughness, improved interface flatness, and to avoid intermixing at the interfaces, each individual layer was engineered by use of a two-stage ion assistance process during magnetron sputter deposition: The first 0.3 nm of each Ti and Cr layer was grown without ion assistance, and the remaining 0.39–0.72 nm of the layers were grown with high ion–neutral flux ratios \( \Phi (\Phi _{\text{Ti}} = 3.3, \Phi _{\text{Cr}} = 2.2) \) and a low energy \( E_{\text{ion}} (E_{\text{Ti}} = 23.7 \) and \( E_{\text{Cr}} = 21.2 \) eV), ion assistance. A maximum soft-x-ray reflectivity of \( R = 2.1\% \) at near-normal incidence (\( \theta = 78.8^\circ \)) was achieved for a multilayer mirror containing 100 bilayers with a modulation period of 1.379 nm and a layer thickness ratio of \( \Gamma = 0.5 \). For a polarizing multilayer mirror with 150 bilayers designed for operation at the Brewster angle, \( 45^\circ \), an extinction ratio, \( R_s/R_p \), of 266 was achieved with an absolute reflectivity of \( R = 4.3\% \). © 2006 Optical Society of America

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1. Introduction

Despite considerable recent effort in research and technology, the limited reflectivity of soft-x-ray optics remains an obvious restriction in the development of soft-x-ray instrumentation. This limitation is severe at near-normal incidence in the high absorption wavelength range of \( \lambda \sim 2.4–4.4 \) nm, the so-called water window. The advancement in the multilayer (ML) mirror optics in this energy range is still beyond the desire, mainly due to the extreme demands on interface roughness, limited material choice, and technical as well as physical limitations in the growth process. The chemical and optical properties of selected materials have a significant influence on reflectance at particular wavelengths. For example, three-dimensional (3-D) transition metals such as Sc, Ti, V, and Ni can be used for high reflectivity normal incidence MLs by utilizing anomalies in optical constants at their respective absorption edges.

This work is an effort to study Ti-based multilayers that can be used as focusing mirrors in tabletop instruments with soft-x-ray sources based on transition and Čerenkov radiation at the Ti–2\( p \) absorption edge at \( E = 452 \) eV (\( \lambda = 2.74 \) nm). These multilayer mirrors can act as reflecting optics both at normal and oblique incidence in any x-ray imaging instrument designed for this particular wavelength, e.g., x-ray microscopes and x-ray telescopes. These mirrors also have potential applications in synchrotron beam line instrumentation as reflection polarizers and monochromators. Previously, Ni–Ti and W–Ti metal systems were investigated by Mertins et al.\(^2\) for near-normal incidence reflectance and transmittance on the basis of the largest possible reflection coefficients\(^3\) of Ni and W at their boundaries with Ti. In our design, Cr was selected in combination with Ti because of a maximum theoretical reflectance of \( \sim 46\% \), calculated by the IMD code\(^4\) by use of Henke optical constants,\(^5\) for semi-infinite Cr–Ti multilayers, which is comparable with the other material combinations.

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just mentioned. Cr has a lower absorption coefficient \( \beta \) compared with Ni and slightly less contrast in the dispersion coefficient \( (\Delta \delta) \), which in turn gives a slightly lower reflectance from a single interface according to

\[
R = \frac{(\Delta \delta)^2 + (\Delta \beta)^2}{4}.
\]  

Although Ni–Ti gives a higher reflectance of approximately \( N \approx 250 \) bilayers (because of the higher contrast in \( \delta \)) and thereafter saturates, Cr–Ti allows more than 250 bilayers to contribute to the reflectivity, and hence the reflectivity increases beyond \( N \approx 250 \) because of the lower overall absorption.7 Therefore, we explored the Cr–Ti material combination to achieve normal-incidence ML mirrors with large \( N \), giving as high reflectivity as possible near the Ti edge.

Even the best-selected material combination (according to the optical, chemical, and physical parameters) exhibit in reality poor mirror performance, mainly restricted by the present inability to fabricate perfect ML interfaces. A highly reflecting mirror requires abrupt and sharp interfaces, preferably of structurally amorphous layers, throughout the ML stack. To have minimal accumulated roughness, improved interface flatness, and to avoid intermixing at the interfaces, a novel technique of modulated ion-assisted growth was used in which each individual layer was engineered by use of two-stage ion assistance. Initially, during the first 0–0.4 nm growth of each layer, very low ion-assistance energy was used to produce an abrupt interface without intermixing. In the final part of the deposition of each layer, higher ion energy was used to create a dense layer with a smooth surface. A detailed description of the scheme has been presented elsewhere.8

Here we describe the interface-engineered growth of smooth Cr–Ti multilayers with abrupt interfaces. We focused mainly on the roughness evolution in multilayers with an increased number of periods, quantitatively and qualitatively investigated by use of x-ray reflection (XRR) and transmission electron microscopy (TEM). Each bilayer is approximately 1.4 nm thick with interface widths near 0.3–0.4 nm. Polarizing power of a ML designed for reflection at the Brewster angle is also investigated for this material system.

A. Experimental Details

A dual-cathode dc magnetron sputter deposition system with circular magnetron sources having unbalanced type-II magnetic configuration with opposite polarities was used to deposit all the MLs. The two 75 mm diameter magnetrons were mounted at off-axis positions and formed an angle of 25° with the substrate normal. An electrically isolated \( \mu \)-metal shield between the magnetrons serves to protect the targets from cross-contamination and also to extend the magnetic field lines closer toward the substrate. This configuration leads to strong magnetic fields from the outer poles extending into the chamber in which they couple to a separate solenoid that surrounds the substrate. The solenoid consists of 220 turns of Kapton-insulated Cu wire \(( \phi = 2 \text{ mm})\) wound on a stainless-steel frame with an inner diameter of 125 mm. The solenoid current was constant at 5 A with a direction that couples the magnetic field of the solenoid to that of the magnetron being used for deposition. These magnetic field lines guide the secondary electrons from the magnetrons to the substrate region to enhance ionization of the working gas in the vicinity of the growing film. This enhanced ion density plays a central role in engineering smooth and abrupt interfaces between growing layers. The substrate is biased with a negative voltage, \( V_s \), to attract a high flux of ions from the surrounding plasma to the growing film in a controlled manner with desired energies. A more detailed description of the deposition system can be found in Refs. 9 and 10. All the depositions were carried out by use of chemically cleaned Si(001) substrates (40 mm \( \times \) 20 mm \( \times \) 0.5 mm) mounted on the electrically isolated substrate table, rotating at a constant rate of 60 rpm and placed at a distance of 120 mm from each magnetron. The background pressure prior to deposition was \( \sim 2 \times 10^{-7} \text{ Torr} \) and a low working sputtering gas pressure of \( \sim 3 \text{ mTorr Ar} \) was maintained during all depositions.

Plasma probe measurements were carried out to obtain a quantitative estimation of the average number of Ar gas ions and their corresponding energy transfer to each deposited atom during each part of the growing Ti and Cr layers. Current–voltage characteristics of the plasma were measured in both regimes dominated by ion currents and electron currents by use of two different electrical probe geometries; a flat stainless-steel probe \((\text{area } A_p = 1.77 \text{ cm}^2)\), and a cylindrical Langmuir probe \((\text{a tungsten wire probe, } 5 \text{ mm long, } 0.25 \text{ mm diameter})\), respectively.

The MLs were intended for the first-order reflections at near-normal incidence and oblique incidence at the Brewster angle of \( \sim 45^\circ \), just below the Ti-2p emission line. Simulations made with the IMD code predicted optimal periodicities of \( \Lambda = 1.379 \text{ nm} \) and \( \Lambda = 1.99 \text{ nm} \), respectively, and layer thickness ratios of \( \Gamma = 0.5 \) for this wavelength. No separate capping layer was used, but growth was designed, on purpose, to end with Cr as the top layer because of its ability to form a passive oxide layer over the highly reactive Ti.

Determination of deposition rates, measurements of layer thickness, and optimization of ion energy as well as multilayer design affirmation were all carried out by measuring Bragg-peak positions and/or intensities from low-angle x-ray reflectivity scans with a line-focus copper anode source \((\text{Cu-K}_\alpha, \lambda = 0.154 \text{ nm operating at } 0.8 \text{ kW})\). Taking into consideration the first-order reflection at high angles \( >5^\circ \), the effect of refraction could be neglected in applying Bragg’s law for determination of bilayer period \( \Lambda \).
We took soft-x-ray reflectivity measurements at the Ti-2p absorption edge by using an ultrahigh-vacuum polarimeter with an energy resolution of approximately \( E/\Delta E = 2500 \) in both \( s \) and \( p \) geometries at beamline UE56/1 at BESSY II. The exact position of the Ti-2p absorption edge was determined by performing a so-called Bragg scan, for which the \( \theta-2\theta \) scans were made to vary photon energies around the absorption edge. These two-dimensional scans were also performed in both \( s \) and \( p \) polarization to determine the polarizing power of the multilayers intended to work at the Brewster angle.

For structural characterization cross-sectional transmission electron microscopy (XTEM) was performed in a CM 20 UT microscope equipped with a LaB\(_6\) filament, operated at 200 kV with a point resolution of 0.19 nm for structural characterization. We prepared cross-sectional samples by chemical thinning and polishing from both sides. Low-angle (4\(^\circ\)) ion milling in a BalTec RES 010 rapid ion etch that operated at 8 kV was used to make the samples electron transparent. A final polishing stage that uses low-energy ions at 2 kV was applied to remove any amorphous surface layer formed in the previous stage.

2. Results and Discussion

By use of magnetron-solenoid magnetic coupling a relatively large negative floating potentials of the substrate, \( V_s = -22 \) V, recorded for both materials, indicated the presence of a large number of secondary electrons and hence a large fraction of ionized Ar atoms in the substrate vicinity. The ion-to-metal flux ratios \( \Phi \) at the substrate for the two magnetrons were \( \Phi_{Ti} = 3.3 \) and \( \Phi_{Cr} = 2.2 \), as determined by electrical probe measurements taken with the known deposition rates \( v \) and assuming nominal densities \( \rho \) of the film as

\[
\Phi = \frac{j_i}{j_n} = \frac{IM}{\rho N_A \mu_A q},
\]

where \( I \) is the ion current, \( M \) is the molar mass of the neutral atoms, \( A_p \) is the area of the probe, \( q \) is the ion charge, and \( N_A \) is Avogadro's constant. The plasma potentials were measured with a Langmuir probe for deposition of the two materials \( V_{p(Ti)} = 1.69 \) V and \( V_{p(Cr)} = -1.29 \) V. The energy of the ions that arrived at the growing surface can thus be determined by

\[
E_{ion} = q(V_p - V_s),
\]

where \( V_p \) is the applied substrate bias potential.

The modulated high-flux low-energy ion-assisted growth was optimized for average ion energies [Eq. (3)] as well as for initial layer thicknesses in the Ti and Cr layers by growing several different MLs that contain 20 bilayers with initial layer thicknesses between 0 and 0.4 nm and with different ion energies in the initial and final part of each layer varied in the range from 0 to \(-40 \) eV. The optimization was based on the comparison of low-angle hard-x-ray reflectance of the multilayer peak, the appearance of Kiessig fringes, and the profile of nonspecular rocking curves. We achieved the best MLs by using a 0.3 nm initial thickness with a 1.7 eV ion and 1.3 eV electron bombardment for Ti and Cr, respectively; the remaining parts of the layers were deposited with 23.7 and 21.2 eV ions, respectively. Figure 1 shows the modulated substrate potential with respect to the plasma potential during growth of each part of the Ti and Cr layers. Figure 1 also shows the various thicknesses and ion-electron energies involved.

The electron bombardment shown for the initial growth of the Cr layer is the result of a large secondary electron irradiation from the sputtering process at the target in combination with a slightly positive substrate potential that attracts the electrons. This high-flux low-momentum bombardment has no advantage in displacing surface atoms and can therefore result in increased roughness. Since this happens in the initial part of each Cr layer, it can be compensated by 21 eV ion bombardment in the final part. Electron irradiation can cause a slight temperature increase of the growing film with a possible thermal interdiffusion as a consequence. Once these conditions were established, all the MLs were grown by use of the same optimal parameters.

The successful growth of Cr–Ti MLs with extremely thin layer thicknesses (<0.7 nm) is illustrated in Fig. 2 by the hard-x-ray reflectivity curve along with a simulation for a multilayer with 100 bilayers. The visibility of 98 Kiessig fringes (distinct destructive interference fringes that are due to the finite thickness of the ML being 100 times the period) is clear evidence of a very high layer conformity. The individual layer thicknesses \( d_{Ti} = 0.697 \) nm and \( d_{Cr} = 0.690 \) nm, corresponding to a modulation period of \( \Lambda = 1.39 \) nm, were determined from simulations, which also revealed an average interface width of \( \sigma \).
Interface roughness, interdiffusion and intermixing are not separable in the simulations. At-wavelength soft-x-ray reflectivity measurements made on the same sample by use of near-normal incidence photon energy of 452 eV, corresponding to the Ti-2p absorption edge, showed a peak reflectivity of 2.1% at $\theta \sim 78.8^\circ$ (Fig. 3). This is a high reflectance considering that the highest reported near-normal incidence reflectivity achieved at this x-ray wavelength is 1.7% at 87$^\circ$ from W–Ti multilayers and even lower for the Ni–Ti system.

A simulation of the soft-x-ray reflectivity by use of the IMD code is shown along the experimental curve in Fig. 3. It is in good agreement with the experiment as well as the hard-x-ray reflectivity results. Here again we achieved the same layer thicknesses of $d_{\text{Ti}} = 0.699$ nm and $d_{\text{Cr}} = 0.689$ nm. However, the interface width of $\sigma = 0.33$ nm measured here differs from the hard-x-ray value of $\sigma = 0.46$ nm. This difference in $\sigma$ (Figs. 2 and 3) is due to different coherence lengths of the two probing x-ray wavelengths used, which consequently have different sensitivities to different types of roughness. Short wavelength x rays (Cu-K$_\alpha$ $\sim 0.154$ nm) with a longitudinal coherence length of $\sim 25$ nm at glancing incidence are more receptive to short range lateral roughness correlation, also known as jaggedness. On the other hand, soft x rays at near-normal incidence, with 20 times longer $\lambda$ and $\sim 1000$ times larger transverse coherence length, are more responsive to long-range lateral correlation up to 10 $\mu$m, often called waviness. Soft-x-ray reflectivity is influenced by atomic scale jaggedness on length scales much shorter than the wavelength, in the same way as continuous intermixing influences hard x rays, i.e., reducing the absolute reflectivity without significant lateral or transverse peak broadening.

In Fig. 4 the TEM cross-sectional image is shown for a ML that has a high structural order, as revealed by hard-x-ray reflectivity characterization and has given the best reflectivity at near-normal incidence in soft-x-ray analyses, as illustrated in Figs. 2 and 3, respectively. The image shows the entire ML stack of 100 bilayers with a modulation period of $\Lambda = 1.39$ nm. Although the atomic scale interface investigation for roughness evaluation in such extremely thin MLs is still not fully possible by electron microscopy, however, the highly ordered thin film layered structure is reasonably clear throughout the growth direction. The first $\sim 30$ layers in the stack exhibit smooth and abrupt interfaces without any significant roughness. Thereafter, a low spatial frequency roughness or waviness starts to evolve. The roughness is correlated up to the surface, but individual layers with well-defined interfaces are clearly distinguished even at the extreme end, near the surface. The occurrence of some large amorphous material areas comes from the ion milling preparation process.

The TEM observations immediately infer that local interface widths are unaffected by the large number of layers in the stack and the major cause of reduced ML quality is an increased low spatial frequency roughness with an increased number of bilayers. Therefore, to investigate the Cr–Ti ML system with respect to the accumulated roughness with an increased number of layers, a series of four MLs with a number of bilayers, $N = 20, 50, 100$, and 200, was grown in a row keeping the same deposition conditions and using the optimum design of modulated ion-assisted growth as described above (Fig. 1). We aimed for the same ML period of $\Lambda = 1.379$ nm and layer thickness ratio of $\Gamma = 0.5$ for all the samples. All four samples were characterized using grazing incidence hard x rays ($\lambda = 0.154$ nm) as well as near-normal incidence soft x rays ($\lambda = 2.74$ nm), investigating both specular reflectivity and non-specular diffuse scattering.

A quite similar behavior for the two probing photon energies is shown in Fig. 5, where the specular re-
flectivity is plotted as a function of the number of bilayers for both hard and soft x rays. For hard x rays, the maximum intensity is evident for the ML with $N = 100$, and when the film thickness is increased by more than $N = 200$, a slight decline in the reflectance curve can be observed. In contrast, the soft-x-ray reflectance already begins to reach a saturation limit at $N = 50$ bilayers. Further addition of bilayers could not enhance the peak reflectance and followed the similar trend of declining as in the case of hard x rays. The fact that the reflectivity saturates before the theoretical optimal value for highest reflectivity and subsequently decreases on adding more bilayers is a clear indication of accumulated interface roughness evolution. Another fact, that the longer wavelength reflectance already saturates at a thickness of $N = 50$ bilayers whereas the hard-x-ray reflectivity saturates at approximately 100, is a consequence of a higher sensitivity of interface roughness and a higher absorption of soft x rays. The smoothest layers and best interfaces located at the bottom of the ML stack near the substrate contribute much less to the overall soft-x-ray reflectance. Moreover, the earlier saturation in reflectivity for soft x rays also indicates the existence of long-range lateral roughness (waviness). Hard x rays, with a shorter coherence length in the lateral direction, are virtually insensitive to lateral roughness with characteristic length scales larger than approximately 25 nm, whereas soft x rays probe up to tens of micrometers.

A better understanding of the reflectivity variations is obtained from analyses of the diffuse scattering around the Bragg peak of the MLs with a different number of bilayers in the stack. Figure 6 shows the soft-x-ray rocking curves (a) along with estimated interface widths (b). The two probing x-ray wavelengths show similar behavior, and we therefore limit the discussion here to the soft-x-ray measurements. An immediate conclusion based on qualitative judgment of the rocking curve data, as shown in Fig. 6 (a), is a decrease in the diffuse scattering width with an increased number of bilayers $N$. Since the width of diffuse scattering is inversely proportional to the lateral correlation length, it can be concluded that low spatial frequency roughness increased in lateral directions when $N$ increased. The presence of smooth and abrupt interfaces by use of high-flux low-energy ion-assisted growth is evident for $N = 20$ bilayers, where almost no diffuse scattering is observed around the specular peak position. An outcome of the addition of 30 bilayers is a sharp increase in reflectance from 0.32% to 2.02%, and a signature of diffuse scattering in the form of shoulders around the specular peak start to appear. Since the intermixing at interfaces is induced during the creation of the inter-

Fig. 4. Cross-sectional HRTEM micrograph of a Cr–Ti ML containing 100 bilayers with a nominal period of $\Lambda = 1.39$ nm.
faces, intermixing is independent of the increased number of bilayers, and the accumulation of roughness of the interfaces is therefore the cause of increased peak shoulders whereas local abruptness of the interfaces is maintained throughout the layer stack.

The existence of increased accumulated roughness is further evidenced by a ML with $N = 100$, where a slight increase in peak reflectance and enhanced peak shoulders appeared, and in multilayer $N = 200$, where the slight decrease in peak reflectance is a consequence of a huge increase in roughness accumulation. An exact quantitative estimation of the roughness accumulating on the growing surfaces is a somewhat complicated task. Figure 6(b) shows the evolution of an average interface width (calculated by simulations of specular reflectivity by use of the IMD code), and nonspecular intensity with an increased number of layers. The average interface width, shown at the left axis, can be seen to increase from $\sigma = 0.26$ to $\sigma = 0.41$ nm as the $N$ increases from 20 to 200 bilayers. Nonspecular diffuse scattering was also estimated by measuring the ratio of integrated intensities occupied by the nonspecular to the specular part of the rocking curves and is represented in Fig. 6 by the dotted curve drawn at the right axis. For $N = 20$ this ratio is only 3%, indicating atomically abrupt and smooth interfaces without any accumulated roughness, but increases rapidly to 79% as $N$ increased to 200 in the same way as the average interface width.

The accumulated roughness in these mirrors and the accompanying saturation in reflectivity suggest that the parameters for interface engineering were optimized with a too high emphasis on the local interface abruptness. This is an effect of using only 20 bilayers for the optimization. It is possible that a higher reflectance from mirrors with more than 100 periods can be achieved if slightly higher ion assistance energy is used that promotes layer smoothness at the expense of a slightly broader interface width.

A ML intended as an analyser for polarized synchrotron radiation was grown with 150 bilayers and characterized by use of the same polarimeter as for the previous normal-incidence soft-x-ray measurements. Figure 7 shows the maxima of both $s$- and $p$-polarization angular reflectivity scans performed at various energies. The resulting curves exhibit their maximum just below the Ti-2p absorption edge with absolute reflectivity of 4.3% for $s$ polarization at 42.2°. At the Brewster angle of $\sim 45°$, the extinction ratio $R_s/R_p$ was 266. A much higher extinction ratio is expected if the reflectivity maximum is made to coincide with the Brewster angle of $\sim 45°$, which could be achieved by making a slightly thinner period of 1.99 nm rather than 2.04 nm. This indicates that Cr–Ti MLs are also suitable as soft-x-ray polarizers.

3. Summary and Conclusions
Interface roughness hinders the achievement of highly reflective normal incidence soft-x-ray optics particularly in the high-energy region where interface width has a severe effect on the achieved reflectance. There are many kinds of roughness and it is
not easy to gain control of, either during growth or when making analysis. We show here that interface engineering by modulated ion assistance with a high ion-to-flux ratio can considerably overcome the problem of intermixing Cr–Ti and to some extent produce abrupt interfaces, which is evident by x-ray reflectivity and electron microscopy in Figs. 3 and 4. The roughness evolution observation in the TEM image supports the conclusion drawn about roughness accumulation from the x-ray reflectivity analysis. At near-normal incidence, at the Ti-2p absorption edge in the water window, a Cr–Ti multilayer with 100 bilayers showed a high reflectance of 2.1%. However, the maximum reflectivity is limited by a correlated low spatial frequency roughness evolution with an increased number of bilayers. Also the multilayer with 150 bilayers exhibited a maximum reflectance of 4.3% near the Brewster angle with an extinction ratio of ~266. The obtained reflectances of 2.1 and 4.3% are comparable or higher than the reflectance of state-of-the-art condenser mirrors used in a tabletop microscope that operates at a longer wavelength where more absorption occurs in the specimen.13 We therefore conclude that the Cr–Ti mirrors are of sufficient quality for implementation of an instrument operating at the Ti-edge.

These results clearly demonstrate the successful implementation of interface engineering by use of ion modulation to make Cr–Ti a competitive system for x-ray mirrors.

References