Design of novel titanium oxide/zinc oxide multilayer mirror for attosecond soft X-rays

To cite this article: K Nagai et al 2011 IOP Conf. Ser.: Mater. Sci. Eng. 24 012021

View the article online for updates and enhancements.

Related content
- Novel TiO2/ZrO multilayer mirrors at 'water-window' wavelengths fabricated by atomiclayer epitaxy
  H Kumagai, Y Tanaka, M Murata et al.
- Self-limiting nature of atomic layer epitaxy of wurtzite thin films obtained from sequentially pressurized Zn(C5H2CH3)2 and H2O vapor pulses on sapphire (001) substrates
  H Kumagai, Y Masuda and T Shinagawa
- Comparison of Surface Roughness Estimations by X-ray Reflectivity Measurements and TEM observations
  Yoshikazu Fujii
Design of novel titanium oxide/zinc oxide multilayer mirror for attosecond soft X-rays

K. Nagai, H. Kumagai and Y. Masuda
3-3-138 Sugimoto, Sumiyoshi-ku, Osaka-shi, Osaka 558-8585, Japan
E-mail: kumagai@a-phys.eng.osaka-cu.ac.jp

Abstract. A novel attosecond multilayer mirror was designed at “water-window” wavelengths (from 2.33 nm to 4.36 nm) using a combination of TiO$_2$ and ZnO, because both rutile TiO$_2$ and wurtzite ZnO can be grown epitaxially together on the same c-plane sapphire substrate in spite of the different crystal structures of the molecule hexagonal units of rutile TiO$_2$, wurtzite ZnO and sapphire. The theoretical calculation of the TiO$_2$/ZnO multilayer mirror indicated that a high reflectivity of 50% was attainable at 2.73 nm and at an incident angle of 17.35° from normal incidence. Moreover, it also indicated that a simple 3-block structure could exhibit a reflectivity of about 15% for a 480-attosecond pulse at a water-window wavelength and thus could be used to control the phase relation.

1. Introduction
Attosecond pulses are inevitably in the extreme ultraviolet (XUV) or even soft-X-ray region. In order to filter out such XUV pulses from the comb of a high-harmonic spectrum and guide and focus them, a special technique is necessary. In particular, various XUV optical elements with multilayer coatings are successfully applied for this purpose [1,2]. One of the most efficient XUV and soft-X-ray optical elements is a normal-incidence multilayer mirror that exhibits a rather high reflectivity and controllable spectral properties. They allow one to achieve high reflectivity of up to 70% but at rather narrow spectral intervals [3]. For the reflection of attosecond pulses, broadband mirrors are necessary.

The multilayer mirror represents a step toward aperiodic multilayer mirrors, albeit with a simple design [4]. The mirror was developed for the spectral region of approximately 40 eV, for which the conversion efficiency for high-order harmonic generation in argon reaches high values, and which is therefore particularly well suited to applications in attosecond metrology. Standard mirrors for the region of approximately 40 eV consist of periodic stacks of only two materials, such as Mo/Si or B$_4$C/Si. A novel multilayer mirror consisting of Mo/Si/B$_4$C was designed [5] and then fabricated using a recently developed three-material technology aimed both at reaching reflectivities of about 20% and at controlling dispersion over a bandwidth covering photon energies between 35 and 50 eV [6].

In order to fabricate mirrors providing a broader frequency band, the shortening of the reflection wavelength of multilayer mirrors should become an important issue. In particular, the development of high-performance normal-incidence multilayer optics for the “water-window” wavelength region between the oxygen and carbon K absorption edges of 2.33 and 4.36 nm, respectively, where water is relatively transmissive and organic materials are absorptive, has been a technical challenge, but it will be a solution to the shortening of the reflection wavelength. The extremely small periods (1.2–2.2 nm) of soft-X-ray reflectors mean that very rigorous specifications must be met with respect to interface roughness and interlayer mixing, because interface roughness on the atomic scale has a substantial effect on soft-X-ray reflectivity. The highest reflectivity achieved at a water-window wavelength ($\lambda =3.18$ nm) and near-normal incidence ($\theta =9^\circ$) was 3.3% in the first half of the 1990s [7], in spite of the various studies that had been carried out in this field. The reason why the reflectivities achieved at water-window wavelengths are so low is that the Fresnel coefficients of materials are so small at these
wavelengths that a large number of bilayers must be used, which means that interface roughness and imperfect interfaces due to interlayer mixing become serious problems.

Recently, Cr/Sc multilayers have been fabricated [8, 9] with normal-incidence reflectivity in the vicinity of 20% for wavelengths near the Sc edge at 3.11 nm. The use of diffusion barriers has also been investigated for few-period multilayers. Such diffusion barriers have been successfully applied to Ni/C/Ti/C [10] and Mo/Si [11, 12] multilayers in the XUV region. As the Cr/Sc multilayers using a B2C diffusion barrier were deposited by conventional magnetron sputtering, a reflectivity of 32% was achieved at 3.11 nm at an angle of 10° from the normal [13]. Cr/Ti and Cr/V multilayer systems have also been investigated. In the case of Cr/Ti, a near-normal-incidence reflectivity of 17% was obtained near the Ti L edge at 2.73 nm [13]. For Cr/V, a near-normal-incidence reflectivity of 9% was obtained near the V L edge at 2.42 nm [13]. These results are very encouraging regarding the possibility of more widespread applications of normal-incidence optics in the water-window range.

The authors have proposed the use of a novel metal oxide multilayer for soft-X-ray reflectors at water-window wavelengths [14], because an oxide multilayer can prevent the formation of an alloy at the interface without any buffer layer, and the absorption of oxygen in oxides is negligible at water-window wavelengths. Moreover, the metal oxide multilayer can be fabricated by atomic layer deposition or atomic layer epitaxy (ALE). These techniques can be used to control surfaces on the atomic scale by sequentially dosing the surface with appropriate chemical precursors and then promoting surface chemical reactions that are inherently self-limiting. We have found that the self-limiting adsorption mechanism is effective in the fabrication of thin oxide films such as aluminum oxide and titanium oxide [15-18]. Moreover, we reported the experimental demonstration of a high reflectivity of over 30% at a wavelength of 2.734 nm and an incident angle of 71.8° from the normal incidence, using novel metal oxide multilayers consisting of titanium oxide and aluminum oxide fabricated by controlled growth by atomic layer deposition with sequential surface chemical reactions [19]. For high-power X-ray processing, crystalline multilayer mirrors might be more useful than those with amorphous layers. One of the authors also demonstrated that the novel oxide superlattice structure of 10-bilayer TiO2/ZnO on a sapphire substrate gave a high reflectivity of 29.4% at 2.74 nm, despite the different crystal structures of the molecular hexagonal units of rutile TiO2, wurtzite ZnO and sapphire [20]. With the layer-by-layer growth nature of ALE, the periodicity in multilayer mirrors can be controlled with high precision [21]. This advantage is also valuable for the fabrication of other functional multilayer structures, such as chirped mirrors, which are useful for compensating the temporal broadening of the X-ray pulse [22].

In this paper, we reported their high reflectivities and the strong possibility of their use as attosecond mirrors.

2. TiO2/ZnO mirror structure

In general, a combination of binary materials with refractive indices that are as different as possible and absorption coefficients that are as small as possible should be selected to obtain high reflectivity. Furthermore, a multilayer fabricated from such materials should satisfy the requirements of minimum interface roughness and interlayer mixing. The complex refractive index is given as [23]:

\[ n = 1 - \delta - i\beta = 1 - \frac{N r_e^2 \lambda^2}{2\pi} (f_1 + if_2). \]

Here, \( N \) is the number density of atoms, \( r_e \) is the classical electron radius, \( \lambda \) is the wavelength of the soft X-rays, and \( f_1 \) and \( f_2 \) are the real and imaginary parts of the complex atomic scattering factor, respectively. The Fresnel coefficients were calculated from the complex refraction indices obtained using complex atomic scattering factors formulated by Henke et al. [24]. The wavelength of approximately 2.73 nm in the water-window wavelengths is negative for the real part of the Fresnel coefficient for titanium, because the titanium L2,3 absorption edge is located at 2.729 nm, which corresponds to a photon energy of 454.4 eV. The real part of the Fresnel coefficient for zinc at this wavelength is relatively high, leading to a large difference between the real parts of the binary Fresnel coefficients. Moreover, the imaginary parts of both the Fresnel coefficients are relatively small. The number densities of Ti, Zn, and O atoms are assumed to be the same as those in rutile TiO2 and wurtzite ZnO. The difference between the real parts of the Fresnel coefficients of the binary oxides is almost the same as that between titanium and zinc. Thus, the combination of titanium oxide and aluminum oxide was selected as the material for a soft-X-ray reflector at 2.74 nm.

Rutile TiO2 can be grown epitaxially on a c-plane sapphire substrate, even though rutile TiO2 has a tetragonal SnO2 structure, which is different from that of sapphire, which has a trigonal Bravais lattice.
with the space group of R-3c [20]. It has also been reported that wurtzite ZnO can be grown epitaxially on a c-plane sapphire substrate despite the different crystal structures of the two-molecule hexagonal unit of wurtzite ZnO and sapphire [20].

Therefore, it is possible to form a multilayer with an artificial superlattice consisting of TiO$_2$ and ZnO thin films on a sapphire substrate. In particular, the crystal structures of (200)-oriented rutile TiO$_2$ and (006)-oriented wurtzite ZnO indicate that the metal layers and oxygen layers are separate. Therefore, the monolayer can comprise a metal layer and an oxygen layer. ALE is suitable for the fabrication of the multilayer, where the adsorption of vapor precursors should automatically stop after the deposition of one monolayer (ML) through the self-limiting mechanism. The thicknesses of monolayers of (200)-oriented rutile TiO$_2$ and (006)-oriented wurtzite ZnO in the crystal structure are 0.2297 nm ($a_0/2=0.459373$ nm/2) and 0.2603 nm ($c_0/2=0.52069$ nm/2), respectively [25]. Consequently, the combination of TiO$_2$ and ZnO has the potential to be made into a very attractive water-window multilayer mirror.

![Figure 1](image1.png)

**Figure 1.** Calculated reflectivities (s-polarization) of (TiO$_2$)$_4$(ZnO)$_2$–period multilayer mirror as functions of wavelength.

![Figure 2](image2.png)

**Figure 2.** Calculated reflectivities (s-polarization) of (TiO$_2$)$_4$(ZnO)$_2$–period multilayer mirror as functions of number of layer pairs.

The reflectivities of the multilayer mirrors were calculated through the Fresnel equation using the complex refractive indices. Figure 1 shows the theoretically calculated reflectivity (s polarization) of the (TiO$_2$)$_4$(ZnO)$_2$ periodic multilayer mirror, where x and y in (TiO$_2$)$_x$(ZnO)$_y$ denote the numbers of
layers in one period for TiO$_2$ and ZnO, respectively. A high reflectivity of 50% is obtainable using 800 pairs of (TiO$_2$)$_4$(ZnO)$_2$ at a wavelength of 2.733 nm and an incident angle of 17.35°, as shown in Fig. 1. Figure 2 shows the calculated reflectivities of (TiO$_2$)$_4$(ZnO)$_2$ at a wavelength of 2.733 nm and an incident angle of 17.35° as a function of the number of layer pairs.

### 3. Theoretical calculations and discussion

High harmonics generated by the nonlinear interaction of ultrashort pulses from a 800-nm high-intensity Ti:sapphire laser with rare gas is currently the most promising way of generating attosecond pulses. The high-harmonic spectrum has a very characteristic shape; it falls off for the first few harmonics, then shows a "plateau" where all the harmonics have the same intensity strength, and finally ends up with a "cutoff" [26]. The cutoff value depends on the IR laser intensity, and it is said that the cutoff will extend the water-window region. The ultrashort pulses are the result of the spectral interference of many high-order harmonics. The phase relation between harmonics is not linear, but there exists inherent group delay dispersion between harmonics that broadens the pulse duration [27]. Chirped mirrors are one of the solutions proposed to overcome this fundamental limitation. Such mirrors must have both a bandwidth to make the high-order harmonics interfere with each other as much as possible and the opposite phase of high-order harmonics that we can control [22]. This induces the particular specification of the multi-block spectral structure based on the multi-period mirrors. In order to design the attosecond mirror in the range of water-window wavelengths, we performed the following theoretical calculations.

Figure 3 shows the theoretical calculations of the reflectivities of [(TiO$_2$)$_3$(ZnO)$_3$]$_{100}$ and [(TiO$_2$)$_4$(ZnO)$_3$]$_{100}$ multilayer mirrors in the 2.6-3.3 nm region and the corresponding single-period structures. In Fig. 3, [(TiO$_2$)$_3$(ZnO)$_3$]$_{100}$ represents 100 bilayers of the (TiO$_2$)$_3$(ZnO)$_3$ single-period multilayer mirror; $\lambda_{3,3}$ and $\lambda_{4,3}$ are 2.730 nm and 3.182 nm, which indicate the reflection wavelength of (3,3)$_{100}$ and that of (4,3)$_{100}$, respectively. $\lambda_{3,3}$ is close to the Ti L absorption edge. The reflectivity at 2.730 nm is 26.3%, while that at 3.182 nm is 6.0%. The reason why the reflection peaks at approximately 2.730 nm are outstanding is the anomalous dispersion around the titanium L absorption edge. As shown in Fig. 3, each theoretical reflection peak has a narrow bandwidth, and there is a wide gap between neighbors. This property is, indeed, undesirable for a broadband mirror. This disadvantage is caused by the discrete thickness of ML owing to the layer-by-layer growth of ALE. However, the adoption of the multi-period structure can solve the above problem.

![Figure 3. Calculated reflectivities of single-period multilayer mirrors. Structures (a) and (b) are [(TiO$_2$)$_3$(ZnO)$_3$]$_{100}$ and [(TiO$_2$)$_4$(ZnO)$_3$]$_{100}$, respectively.](image)

In order to control the reflection wavelength precisely, a multi-period structure should be proposed [21]. The reflection wavelength of the multi-period mirror is determined by the combined ratio of the periodic layers. With the use of this simple combination rule, multi-period mirrors at the selected wavelength are designed. Figure 4 indicates two examples of the calculated reflectivity of multi-period mirrors. In Fig. 4, a reflection peak midway between $\lambda_{3,3}$ and $\lambda_{4,3}$, that is $(\lambda_{3,3}+\lambda_{4,3})/2 = 2.956$ nm, is
produced by a combination of \((\text{TiO}_2)_3(\text{ZnO})_3\) and \((\text{TiO}_2)_4(\text{ZnO})_3\) in the ratio of 1:1. Correspondingly, a 
\((8\lambda_{3,3} + \lambda_{4,3})/9 = 2.780 \text{ nm}\) mirror is obtained from \((\text{TiO}_2)_3(\text{ZnO})_3:(\text{TiO}_2)_4(\text{ZnO})_3 = 8:1\). It is important that one period of \((\text{TiO}_2)_4(\text{ZnO})_3\), should be inserted uniformly into the major period, \((\text{TiO}_2)_3(\text{ZnO})_3\), to obtain a higher reflectivity at 2.78 nm. By this method, the wavelength of the reflection peak, can be controlled fractionally.

**Figure 4.** Calculated reflectivities of multi-period mirrors. (a) and (d) show single-period structures such as \([(\text{TiO}_2)_3(\text{ZnO})_3]_{100}\) and \([(\text{TiO}_2)_4(\text{ZnO})_3]_{100}\), respectively. (b) and (c) show multi-period structures such as \{[(\text{TiO}_2)_3(\text{ZnO})_3][\text{(TiO}_2)_4(\text{ZnO})_4]_{11}\} and \{"[(\text{TiO}_2)_3(\text{ZnO})_3][\text{(TiO}_2)_4(\text{ZnO})_4]_{150}\}, respectively.

**Figure 5.** Schematic blocks of the multi-period mirror.

Next, a multi-period structure such as the so-called “chirped mirror” is useful for broadband reflection in the water window. This structure is based on the depth-graded stacking of some blocks that have different wavelengths of which reflections peak. Figure 5 shows a simple 3-block structure of the multi-period mirror. The 165-period structure of \((\text{TiO}_2)_3(\text{ZnO})_3\) in the 1st block provides a reflection wavelength \(\lambda_{3,3}\) of 2.730 nm. The 60-period structure of a combination of \((\text{TiO}_2)_3(\text{ZnO})_3\) and \((\text{TiO}_2)_4(\text{ZnO})_3\) in the ratio of 19:1 in the 2nd block provides a reflection wavelength \(\lambda_{3,3}\) of 2.753 nm.
The 44-period structure of a combination of (TiO$_2$)$_3$(ZnO)$_3$ and (TiO$_2$)$_4$(ZnO)$_3$ in the ratio of 10:1 in the 3rd block provides a reflection wavelength $\lambda_{3,3}$ of 2.771 nm.

**Figure 6.** Calculated reflectivities of 3-block structure of multi-period attosecond mirror in wavelength region from 2.7 nm to 2.83 nm.

**Figure 7.** Calculated phase relation of 3-block structure of multi-period attosecond mirror in wavelength region from 2.7 nm to 2.83 nm.

**Figure 8.** Fourier transformation of calculated reflectivity shown in Fig. 6.

Figure 6 shows the calculated reflectivity and then Figure 7 shows the phase relation of the 3-block structure of the multi-period mirror. It is noted that the chirped mirror can give the reflectivity of about
15% over a wide bandwidth covering from 2.73 nm to 2.89 nm in the water window. The full bandwidth at half-maximum is 0.03 nm, which is much larger than that of the single-period structure. As shown in Fig. 8, the shortest pulse of 480 attosecond is obtainable theoretically by Fourier transformation of the calculated reflectivity shown in Fig. 6, when it can interfere with each other over the spectral range in this mirror in phase. By varying the number of blocks and the thickness of the multilayers, phase variations and reflectivities can be designed as desired.

4. Conclusions
We have proposed a novel TiO$_2$/ZnO multilayer mirror by an atomic layer epitaxy technique to obtain high-reflection robust mirrors for attosecond soft X-rays at water-window wavelengths, as we have found that both rutile TiO$_2$ and wurtzite ZnO can be grown epitaxially on a c-plane sapphire substrate despite the different crystal structures of the molecular hexagonal units of rutile TiO$_2$, wurtzite ZnO and sapphire. The layer thickness of the multilayer mirror can be precisely controlled by ALE controlled growth with sequential surface chemical reactions. This is advantageous for forming the artificial superlattice multilayer of TiO$_2$/ZnO on sapphire (001), which has reflection planes where metal layers or oxygen layers are alternating. The theoretical calculation of the periodic TiO$_2$/ZnO multilayer mirror indicated a high reflectance of over 50% at a wavelength of 2.73 nm and an incident angle of 17.35° from the normal incidence. Moreover, it also indicated that a simple 3-block structure of the multi-period mirror could exhibit a reflectivity of about 15% for a 480-attosecond pulse at a water-window wavelength and thus the phase relation could be controlled.

References