Soft x-ray reflectometry, hard x-ray photoelectron spectroscopy and transmission electron microscopy investigations of the internal structure of TiO$_2$(Ti)/SiO$_2$/Si stacks

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Abstract

We developed a mathematical analysis method of reflectometry data and used it to characterize the internal structure of TiO$_2$/SiO$_2$/Si and Ti/SiO$_2$/Si stacks. Atomic concentration profiles of all the chemical elements composing the samples were reconstructed from the analysis of the reflectivity curves measured versus the incidence angle at different soft x-ray reflection (SXR) photon energies. The results were confirmed by the conventional techniques of hard x-ray photoelectron spectroscopy (HXPES) and high-resolution transmission electron microscopy (HRTEM). The depth variation of the chemical composition, thicknesses and densities of individual layers extracted from SXR and HXPES measurements are in close agreement and correlate well with the HRTEM images.

Keywords: titanium dioxide, metallic titanium, thin films, interface, soft x-ray reflectometry (SXR), HXPES, HRTEM

1. Introduction

Nowadays, nanometer-thin films and multilayer coatings find multiple applications ranging from gate oxide in microelectronic devices to x-ray mirrors. In many cases, the properties of these layers govern the performance of the fabricated device, mandating strict structural and chemical control of the films and their interfaces. Note that the thickness of an individual film can be as small as a fraction of a nanometer. Hence, the interlayers (their extension and composition) generated at the interface between two different substances play increasingly important roles owing to processes such as interdiffusion, chemical reactions and implantation during the synthesis of films. In particular, the formation of interlayers may have a detrimental effect on the electronic properties of interfaces, for instance, precluding one from reaching the quantum-confinement regime in nanoelectronic structures [1–3] or a catastrophic drop in reflectivity of short-period multilayer x-ray mirrors [4, 5]. It is clear that one needs to develop analytical methods suitable
for the analysis of both nanometer-thin films and interlayers formed at their interfaces.

In this work we developed a mathematical analysis method of reflectometry data and applied it to the investigation of the internal structure of TiO$_2$(Ti)/SiO$_2$/Si stacks. X-ray reflectometry is an efficient characterization method of internal material structure including buried interfaces. The reflectivity curve measured as a function of the incidence angle contains the interference pattern generated by the x-ray wave reflected from different features of the dielectric constant profile and allows the reconstruction of this profile with high depth resolution. Measurements of the reflectivity curves at different soft x-ray reflection (SXR) photon energies can yield depth distribution of all the chemical elements composing a sample.

The SXR results were compared with the results of two independent techniques—hard x-ray photoelectron spectroscopy (HXPES) and high-resolution transmission electron microscopy (HRTEM).

2. Experiment

TiO$_2$ films are being extensively studied because of their interesting chemical, electrical and optical properties resulting in widespread applications, e.g., in catalysis, photocatalysis, dye-sensitized photovoltaic cells, gas sensors [6–9] and pharmaceuticals [10–12]. Besides, TiO$_2$ nanofilms are widely used as protective layers for very large-scale integrated (VLSI) circuits and as antireflective (AR) coatings for optical elements and planar waveguides. TiO$_2$ capping layers also protect Mo/Si multilayer structures against oxidation during extreme UV lithography exposure.

We investigated two samples: TiO$_2$ (sample 1) and metallic Ti (sample 2) films of about 10 nm thickness, which were deposited by radio-frequency (RF) and dc magnetron sputtering, respectively, on superpolished Si(111) space substrates covered with a 2-nm-thick natural oxide. Ar was used as working gas.

The HXPEs experiments were performed using the HIKE station at the KMC-1 beamline at the BESSY II synchrotron light source of the Helmholtz–Zentrum Berlin. This experimental setup is equipped with a high-resolution hemispherical electron analyzer optimized for high-energy electrons (VG Scienta R4000). The analyzer is installed at 90° to the incident beam and thus the data acquisition is performed in normal emission of electrons from the sample surface and grazing incidence of the photon beam. The spectrometer resolution was set to 0.25 eV while the KMC-1 double-crystal monochromator provided a 0.4 eV bandwidth at 3010 eV. Further details about the experimental setup can be found in [13, 14].

The soft x-ray reflectivity curves were measured as a function of the incident angle at different SXR photon energies $E$. The measurements were performed using s-polarized synchrotron radiation in the reflectometry setup of the optics beamline at BESSY II [15, 16]. The accuracy of the energy scale was 10 meV. All the curves were measured with an angular accuracy of 0.001°. The total intensity of the reflected beam was monitored using a GaAsP diode (4×4 mm$^2$), coupled with a Keithley 617 electrometer. We used a system of absorption filters to reduce high diffraction orders in the incident beam.

3. Results and discussion

3.1. Reflectometry

The reconstruction of the depth profile of dielectric constant $\varepsilon(z)$ from angular reflectivity measurements $R(\theta)$ is a well-known inverse problem of reflectometry. However, even for hard x-rays or neutrons, where radiation absorption can often be neglected, such reconstruction is ambiguous in the absence of additional a priori information about the sample [17–20].

The simplest and most widely used approach to the inverse problem is modeling the $\varepsilon(z)$ distribution with a function of several unknown parameters, which are found using a least-squares fit to experimental data. This approach assumes that the internal structure of the sample is known a priori. The main advantage of this approach is that it works, provided that an adequate sample model is available [17]; otherwise, one should use a model-independent approach to solve the inverse problem. Several free-form approaches have been developed for reconstructing $\varepsilon(z)$ from x-ray or neutron reflectivity data. General ones include the maximum entropy method, the Bayesian spectral analysis [17], the parameterization of $\varepsilon(z)$ distribution using cubic B splines or sinus/cosine basis [18], and an iterative approach based on a linearization of expression for the reflectivity with respect to the unknown part of the potential (dielectric function) [21]. Nevertheless, the problem of ambiguity remains unsolved.

Bengu et al [22] have developed an approach allowing the discovery of a set of physically sound solutions. The approach is based on the genetic algorithm used together with phase inversion to impose a set of general constraints that will limit the number of possible solutions. Similarly, the approach developed in [20] allows us to select, among a great number of possible solutions, those providing the desired (modeled) reflectivity amplitude behavior at large $q=k \sin \theta$ (where $k=2\pi/\lambda$) including unphysical values $q>k$.

All the approaches mentioned above have been developed to reconstruct $\varepsilon(z)$ at the working wavelength and do not allow predicting $\varepsilon(z)$ at another wavelength. Below, we discuss a procedure to determine the depth distribution of atomic concentration of all the chemical elements in a sample and to calculate the dielectric function at any wavelength.

The reflectivity of a layered sample is determined entirely by the depth distribution of the dielectric permittivity $\varepsilon(z,E)$, which also depends on the photon energy $E$. If the sample consists of several chemical elements $A, \ldots, B$, the dielectric permittivity distribution in the SXR region can be represented [23] as $1-\varepsilon(z,E) \sim E^{-2}[C_A(z)f_A(E)+\cdots+C_B(z)f_B(E)]$, where $C_j(z)$ is the atomic concentration profile and $f_j(E)$ is the complex atomic scattering factor of the $j$th element. The values of Re($f$) and Im($f$) characterize refraction and absorption of the SXR radiation, respectively. Below, we
assume that the chemical elements composing a sample are known a priori. The values of \( f_j(E) \) were tabulated as a function of energy for all the chemical elements and can be found, e.g., at the website of the Center for X-Ray Optics (Berkeley) [24]. Our approach is based on the measurement of the reflectivity \( R(\theta, E) \) versus the incident angle \( \theta \) at different photon energies, where the atomic scattering factors take different values. Then the atomic concentration profiles \( C_j(z) \) of all the involved elements are reconstructed by fitting all the experimental curves simultaneously. The first attempt demonstrating such a reconstruction is described in [25].

Note that this problem might have several solutions, as we want to deduce several unknown functions \( C_j(z) \), and that radiation absorption cannot be neglected. In this study, we apply the well-known philosophical principle of Ockham’s razor: when several models describe some physical phenomenon, use the simplest one consistent with the experimental data (see also [20]). In other words, we consider a sequence of models of progressively increasing complexity until the necessary accuracy is achieved in fitting experimental data.

Figure 1 (circles) shows the measured reflectivity of sample 1 versus the grazing angle at different energies of the incident beam. Solid curves show the result of fitting with the three-layer model (C/TiO\(_2\)/SiO\(_2\)/Si) after refinement using the merit function (3). The reflectivity curves at \( E = 500 \) and 620 eV are shifted by factors of 10 and 100, respectively.

The simplest model of sample 1 is a uniform TiO\(_2\) film placed on a uniform Si substrate. The four fitting parameters are the thickness and density of the film, the root-mean-square (rms) roughnesses \( \sigma \) of the Si substrate and film surface. The substrate density (2.42 g cm\(^{-3}\)) is assumed to be known.

First of all, note that the angular width of the detector entrance aperture was about 2\(^\circ\) in our experiments. It indicates that the radiation scattered by the long-scale conformal roughness with the large correlation length in the interface plane was detected when measuring the reflectivity. Hence, the short-scale roughness, which is usually nonconformal (see, e.g. [26]), affects only the experimental reflectivity. The effect of the short-scale nonconformal roughness on the reflectivity can be described in two equivalent ways: by introducing the Nevot–Croce factor [27] to the reflectance amplitude of each interface or by considering a smooth variation of the dielectric constant at each interface. If the roughness height is distributed in accordance with the normal law, the ‘effective’ transition layer, formed near a rough interface as a result of short-scale roughness averaging, has the following dielectric function:

\[
\varepsilon(z) = \frac{\varepsilon_A + \varepsilon_B}{2} - \frac{\varepsilon_A - \varepsilon_B}{2} \text{erf}\left(\frac{z}{\sigma \sqrt{2}}\right).
\]

Here, \( \varepsilon_A \) and \( \varepsilon_B \) are the dielectric permeabilities of the neighboring materials, \( \sigma \) is the interface width, and \( \text{erf}(x) \) is the error function. If the scattering of SXR radiation by the interfacial roughness is not analyzed in the experiment, as in our case, it is impossible to distinguish the contributions to the reflectivity from small-scale roughness and from the real transition layer formed between neighboring materials due to interdiffusion, implantation and chemical reactions. Thus, the \( \sigma \) values below characterize the cumulative effect of small-scale roughness and the transition layer.

Figure 2 shows fitting results of the reflectivity curves of sample 1 using the simplest approach, the well-known Paratt formalism [28]. When the sample is considered as TiO\(_2\) on Si (‘single layer’), the agreement with the experiment is reasonable for \( E = 97 \) eV, but not for \( E = 340 \) eV.

A more complex model takes into account the oxide layer on the Si substrate. Therefore, in the second step of our procedure, we fit experimental curves using the two-layer model TiO\(_2\)/SiO\(_2\)/Si. As above, the fitting parameters are the thickness and density of all the layers as well as the rms roughness \( \sigma \) of all the interfaces. Note that in this model, the \( \sigma \) value of the SiO\(_2\)/Si interface characterizes a gradual variation of the silicon and oxygen concentrations with the substrate depth rather than a rough boundary between the Si substrate and the oxide layer. Figure 2 reveals that with the two-layer model, the accuracy of fitting is improved by a factor of two in the minimum of the reflectivity curve at \( E = 97 \) eV, while it is practically unchanged at \( E = 340 \) eV.

The next approximation includes an adhesion layer, which is always formed on any surface and mostly consists of hydrocarbons and water. For simplicity, we assume that the adhesion layer consists of carbon only. Figure 2 reveals that while introducing the adhesion layer does not affect the reflectivity at \( E = 97 \) eV, the three-layer C/TiO\(_2\)/SiO\(_2\)/Si...
model significantly improves the fit for \( E = 340 \) eV. This energy lies just above the carbon K-edge, where the absorption increases sharply.

Thus, the three-layer model describes the whole set of reflectivity curves reasonably well. Figure 3(a) shows the deduced depths distribution of atomic concentrations, where we used equation (1) to describe the transition layer between the neighboring materials. The thicknesses of the TiO\(_2\) film and SiO\(_2\) oxide layer were calculated as 9.84 and 2.25 nm, respectively. For comparison, the values found with the two-layer model are 9.81 and 2.30 nm. This difference can be taken as an uncertainty of modeling, which does not affect the two-layer model.

The rms roughnesses of the film surface and substrate surface are both about 0.35 nm. As mentioned above, the \( \sigma \) value of the SiO\(_2\)/Si interface (0.41 nm) describes a smooth variation of oxygen concentration with the substrate depth rather than the interface roughness. The adhesion carbon layer is thin (1.29 nm) and loose (maximum density 1.26 g cm\(^{-3}\)). The \( \sigma \) value of the external surface of the adhesion layer (0.46 nm) describes both the roughness and a gradual decrease in the carbon density into vacuum.

The deduced TiO\(_2\) and SiO\(_2\) layer thicknesses as well as the SiO\(_2\) layer density agree well with those deduced from the HXPES measurements (see below), while the TiO\(_2\) layer density is about 13\% too low. The reason for the discrepancy is yet unclear. It may be related to the inaccuracy in the value of the inelastic mean free path of photoelectrons in TiO\(_2\) and to the use of an oversimplified model in the HXPES analysis (neglecting adhesion layer and interfacial roughness).

The next step of the analysis is numerical refinement of the obtained solution to describe quantitatively all the minor features of the measured reflectivity curves. We based the refinement procedure on the concept of maximum entropy, which was previously used to process hard x-ray and neutron reflectivity curves as well as the HXPES data (see, e.g. [17, 29] and references therein). The generalized Shannon–Jaynes entropy (negative function) is given by [30]

\[
S = \sum_{i,j} \left[ C_j(z_i) - C_j^{(0)}(z_i) - C_j(z_i) \log \left( \frac{C_j(z_i)}{C_j^{(0)}(z_i)} \right) \right],
\]

(2)

where \( C_j(z_i) \) is the concentration of the \( j \)th element in the \( i \)th pixel of the digitized reconstruction of \( C_j(z) \), and \( C_j^{(0)}(z) \) is the default model with respect to which the entropy is measured. In our case, \( C_j^{(0)}(z) \) is the solution obtained with the three-layer model, and if we set \( C_j(z) = C_j^{(0)}(z) \), the entropy is equal to zero. The method is based on finding a \( C_j(z) \) solution, which simultaneously provides an accurate fit of experimental reflectivity curves and corresponds to the maximum entropy. If \( C_j(z) \) is close to \( C_j^{(0)}(z) \), the entropy (2) can be written as

\[
S \approx -\frac{1}{2} \sum_{i,j} \left[ C_j(z_i) - C_j^{(0)}(z_i) \right]^2 / C_j^{(0)}(z_i).
\]

Therefore, we used the following merit function when fitting the measured reflectivities:

\[
MF = \sum_{k,m} \left[ \log R_{\exp}(\theta_k, E_m) - \log R_{\text{calc}}(\theta_k, E_m) \right]^2 + Q \sum_{i,j} \left[ \frac{C_j(z_i) - C_j^{(0)}(z_i)}{C_j^{(0)}(z_i)} \right]^2,
\]

(3)

where the parameter \( Q \) is varied to improve the fitting. Summations over \( i \) and \( j \) are carried out for all the \( z \) points (150 in our calculations) and all the chemical elements composing the sample (C, O, Si and Ti). Therefore, the total number of fitting parameters was 600. Summations over \( m \) and \( k \) are carried out for all the photon energies and grazing angles of incident radiation.

The solid curves in figures 1 and 2 show the fitting results. While the agreement between the calculated and measured curves is almost perfect, the refined concentration distributions (figure 3(b)) reveal that the use of the merit function in form (3) resulted in nonphysical oscillations. They can be reduced by increasing the parameter \( Q \) in equation (3), but at the expense of worsening the fit quality. Therefore,
Figure 3. Reconstructed concentration profiles of chemical elements composing sample 1. Simulations were performed using the three-layer model (C/TiO$_2$/SiO$_2$/Si, no refinement) (a) and after refinement using the merit function (3) (b) or (4) for $n = 1$ (c), $n = 2$ (d) and $n = 3$ (e).

instead of (3), we used the following merit function

$$\text{MF} = \sum_{k,m} \left[ \log R_{\text{exp}}(\theta_k, E_m) - \log R_{\text{calc}}(\theta_k, E_m) \right]^2 + Q \sum_{i,j} \left[ \frac{d^\alpha}{dz} \left( C_i(z_j) - C_i^{(0)}(z_j) \right) \right]^2,$$

where we added a small positive number $\alpha$ into the denominator to overcome the problem of dividing by zero.

Note that in the merit function (3), the measure of proximity of the $C_j(z)$ solution to the default one $C_j^{(0)}(z)$ is the difference between concentrations $C_j(z) - C_j^{(0)}(z)$, while it is the difference in their derivatives $d^n C_j/dz^n - d^n C_j^{(0)}/dz^n$ in the merit function (4).

Figures 3(c)–(e) show the refined concentration distributions for $n = 1$, 2 and 3, respectively. They do not contain the nonphysical oscillations present in figure 3(b). The distributions are very similar to each other and to the default distributions of figure 3(a). They contain two major features. Firstly, oxygen (water) appears in the adhesion layer placed on the top of the sample, the carbon density being reduced. Secondly, the concentration of oxygen increases slightly at the top of the Si substrate (at $z \sim 13$ nm) as
Figure 4. Measured reflectivity of sample 2 (circles) versus the grazing angle at different energies of the incident beam. Solid curves show the result of fitting with the three-layer model (C/TiO$_2$/TiO$_x$/SiO$_2$/Si) after refinement using the merit function (4) for $n = 1$. The reflectivity curves at $E = 500$ and 620 eV are shifted by factors of 10 and 100, respectively.

Figure 5. Measured reflectivity of sample 2 (circles) versus the grazing angle at $E = 248$ eV. The curves present simulations with the three-layer (C/TiO$_2$/SiO$_2$/Si) and four-layer (C/TiO$_x$/TiO$_2$/SiO$_2$/Si) models. The results of the four-layer model were further refined using the merit function (4) with $n = 1$.

Figure 6(a) shows the depth distributions of chemical elements reconstructed with the use of the four-layer model. As expected, the upper part of the Ti layer is oxidized. The oxygen concentration decreases gradually inside the Ti layer to about 8 relative percent ($x = 0.08$). The total thickness of the Ti-containing layer is 11.7 nm, while the HXPES analysis yields 13.8 and 13.5 nm for the five-layer and three-layer models, respectively. However, if we take into account the concentration spread near interfaces due to small-scale roughness averaging, the total thickness of the Ti-containing layer becomes 13.5 nm in full agreement with the HXPES results. The maximum density of the TiO$_2$ layer (3.97 g cm$^{-3}$) and maximum partial density of Ti inside the sample (4.43 g cm$^{-3}$) are close to those of the bulk materials and to the value deduced by HXPES.

The rms roughness of the substrate surface (0.3 nm) for sample 2 is practically the same as that for sample 1; however, the rms roughness of the external surface (0.62 nm) is almost two times larger than that for sample 1. This roughness increase is common for the oxidation of metallic surfaces [31].

The most interesting feature observed in the reconstructed concentration distribution is a very small thickness (0.62 nm) of the SiO$_2$ layer on the Si substrate as compared with that for sample 1. This layer is not seen at all in the Si concentration profile in figure 6(a) due to the formation of an ‘effective’ transition layer, as short-scale roughness averaging is included in the calculations. The maximum density of the SiO$_2$ layer (3.97 g cm$^{-3}$) and maximum partial density of Si inside the sample (4.43 g cm$^{-3}$) are close to those of the bulk materials and to the value deduced by HXPES.

Figure 6(b) results in very small changes in the concentration profiles. Oxygen appears in the adhesion layer of sample 2, but the oxygen peak is less clear than that in sample 1 because of the oxygen binding by the titanium film. In addition, the oxygen concentration is enhanced in the Ti layer near the substrate ($z \sim 12.5$ nm).

3.2. Hard x-ray photoelectron spectroscopy investigations

In addition to SXR, we carried out chemical analysis of the samples by HXPES. A key factor in any photoemission...
experiment is the sample depth sensitivity. It is traditionally related to the inelastic mean free path (IMFP, $\lambda_i$) [32], which is defined as the average distance that an electron with a given kinetic energy travels between successive inelastic collisions. Tanuma et al reported a formula (designated TPP-2M) for the IMFP in any material [33].

In the case of a uniform overlayer of thickness $d$, the intensity of photoelectrons emitted from the substrate, if the effects of elastic scattering can be ignored, is given by

$$I = I_0 e^{d/\lambda_i \cos \theta},$$  \hspace{1cm} (5)

where $I_0$ is the signal from the bare substrate ($d = 0$), $\theta$ is the angle of photoelectron emission from the surface (with respect to the surface normal), and $\lambda_i$ is the IMFP for the overlayer material.

According to [34, 35], if elastic scattering is taken into account, the effective attenuation lengths (EAL, $L_e$) should be used in equation (5) instead of the IMFP. The EAL is defined in [36, 37] as a function of $d$ and $\theta$ rather than simply an optical constant of the material like the IMFP. According to Powell and Jablonski [37], the ratio $L_e/\lambda_i$ can be considered as a constant with a value of about 0.75 for $\theta < 60^\circ$. Therefore, equation (5) can be used in further calculations for $\theta < 60^\circ$.

Figure 7 shows the dependence of $P(d) = I/I_0$ as a function of the TiO$_2$ film thickness for $\theta = 5^\circ$, 15$^\circ$, 45$^\circ$ and 60$^\circ$, calculated for a photon energy of 3010 eV. $P(d)$ decreases significantly with $\theta$ above 15$^\circ$. Note that TiO$_2$ films can be probed to a 10 nm in depth at this energy when $\theta$ is scanned between 0 and 60$^\circ$.

Figure 8 shows the Ti 2p photoelectron spectra from samples 1 and 2 measured at an excitation energy of 3010 eV. For clarity, all the spectra are normalized to the background. Their analysis reveals the following: (i) the spectra from sample 1 measured at different emission angles are indistinguishable; (ii) the spectra from the two different samples are very similar and contain a doublet A–B with a spin–orbit splitting of 5.7 eV, a 1 : 2 intensity ratio of the components and the same binding energy in both samples, which correlates well with the parameters of the Ti 2p peak in TiO$_2$ [38]; (iii) sample 2 shows an additional feature C at 453.8 eV, and the intensity of this peak decreases with increasing emission angle. Obviously, a fraction of the Ti film in sample 2 is TiO$_2$.

The full-width at half-maximum (FWHM) of feature B is 1.1 eV in all the spectra from sample 1. The same width is observed for sample 2 at 60$^\circ$ (figure 8(b)), but it increases with decreasing emission angle (table 1).

Figure 9 shows the fitted Ti 2p photoelectron spectra from sample 2 recorded at different excitation energies and emission angles. The spectrum of figure 9(d) was taken from the same sample, but at a different beamline at BESSY II (Russian–German Beamline RGBL) where lower excitation energies were available, e.g., 800 eV.

From the analysis of the fitting components, the feature C at 453.8 eV can be assigned to the Ti$^{5+}2p_{3/2}$ peak of metallic Ti [38, 39]. The spin–orbit splitting Ti$^{5+}2p_{3/2}$ -Ti$^{5+}2p_{1/2}$ is
Figure 8. Ti 2p photoelectron spectra from samples 1 (a) and 2 (b) measured at an excitation energy of 3010 eV and different emission angles.

Figure 9. Experimental and simulated Ti 2p photoelectron spectra from sample 2 for different excitation energies and emission angles: (a) $E = 3010$ eV and $5^\circ$, (b) $E = 3010$ eV and $60^\circ$, (c) $E = 2010$ eV and $60^\circ$, (d) $E = 800$ eV and $0^\circ$.

6.0 eV and the intensity ratio between the components is 1 : 2. These facts agree well with the characteristics of the 2p peak in metallic Ti [38]. The Ti$^{2+}$2p$_{1/2}$ and Ti$^{4+}$2p$_{3/2}$ peaks have similar energies, which is why the FWHM of feature B increases with the probing depth. Other peaks from the low (TiO$_x$, x < 4) oxidation states of titanium lie between the Ti$^{2+}$2p$_{3/2}$ and Ti$^{4+}$2p$_{3/2}$ features. Fitting indicates that the Ti$^{0}$ peaks are dominant and are twice stronger than TiO$_4$ components. The intensities of metallic titanium peaks decrease with increasing emission angle (figures 9(a) and (b)) and with decreasing excitation energy from 3010 to 2010 eV at 60° emission angle (figure 9(c)); these peaks disappear at 800 eV and normal incidence (figure 9(d)). Considering that larger emission angles correspond to a smaller probing depth, we conclude that a TiO$_2$ film has formed at the surface of sample 2, preserving metallic titanium between the oxide
film and substrate. This behavior is seen in all the titanium core-level spectra: Ti 2s, 3s and 3p (figure 10). In all the spectra from sample 2, the Ti\(^{0}\) component appears and grows as the emission angle decreases.

Figure 11 shows the Si 2p spectra measured at different emission angles for both samples. A prominent Si\(^{0}\) peak centered at 99.3 eV, which according to [38, 40] reflects the Si\(^{2+}\) state, is seen only for sample 1. This sample has a SiO\(_2\) layer sandwiched between the TiO\(_2\) film and the substrate. The SiO\(_2\) signal is very small at emission angle 5° in sample 2 (figure 12). Metallic Ti is famous for its reactivity with oxygen [41], and thus, oxygen diffusion from the SiO\(_2\) layer to Ti is expected.

This analysis shows that a thick TiO\(_2\) film is created on top of the Ti layer in sample 2, which can then be presented as TiO\(_2\) [TiO\(_x\) ]Ti/SiO\(_2\) /Si.

To determine the thicknesses of individual layers, we took into account the results [42–44] and made the following assumptions: the sample is amorphous or polycrystalline, inelastic scattering is small, refraction of escaped electrons is small, photon penetration depth does not depend on the material, sample surface is smooth at the atomic scale, acceptance angle of the analyzer is small, sample is homogeneous in the XY-plane, and HXPEs peak area can be estimated accurately in spite of background, asymmetry, instrumental resolution and overlap with other peaks. Within this model, the recurrent formula for the intensity of an HXPEs peak from an \(n\)-th layer can be expressed as

\[
F_n(\theta) = A_{\text{exp}}(\theta) \sigma_n c_n \lambda_n \gamma_n (1 - e^{-d_n \cos \theta}) \prod_{i=1}^{n-1} e^{-d_i \cos \theta}.
\]  

Here, \(n\) denotes the layer number (\(n = 1\) corresponds to the upper layer), \(\sigma_n\) is the photoelectric cross-section, \(\lambda_n\) is the inelastic mean free path, \(\gamma_n\) is the orbital angular symmetry factor, \(c_n\) is the atomic concentration, and \(d_n\) is the thickness of the \(n\)-th layer. The constant \(c(z)\) has the same value for each layer, \(A_{\text{exp}}(\theta) = TA \cos \theta\), \(T\) is a constant accounting for the geometry of the experimental setup, and \(A\) is the analyzed part of a sample.

According to the HXPEs analysis, sample 1 can be presented as the three-layer stack TiO\(_2\) /SiO\(_2\) /Si. Therefore, the Ti\(^{2+}\) 2p, Si\(^{2+}\) 2p and Si\(^{0}\) 2p peaks correspond to the TiO\(_2\) layer, SiO\(_2\) layer and Si substrate, respectively. According to equation (6), the intensities of these peaks can be
expressed as

\[
F_{\text{Ti}^{2+}2p}(\theta) = A_{\text{exp}}(\theta) \sigma_{\text{Ti}^{2+}2p} \rho(\text{TiO}_2) \lambda(\text{TiO}_2) \, (\text{TiO}_2) \, (\theta)
\]

\[
F_{\text{Si}^{2+}2p}(\theta) = A_{\text{exp}}(\theta) \sigma_{\text{Si}^{2+}2p} \rho(\text{SiO}_2) \lambda(\text{SiO}_2) \, (\text{SiO}_2) \, (\theta)
\]

\[
F_{\text{Si}^{0}2p}(\theta) = A_{\text{exp}}(\theta) \sigma_{\text{Si}^{0}2p} \rho(\text{Si}) \lambda(\text{Si}) \, (\text{Si}) \, (\theta)
\]

where \(\sigma\) and \(\gamma\) are tabulated in [45], \(\lambda\) can be calculated with the TPP-2M formula [33] and \(c\) is related to the density of the material. To determine \(\lambda\) and \(c\), we took bulk densities from the database of Lide et al [46]. Because the density of a thin layer \(\rho\) can differ from that of a bulk material, a fitting procedure was applied. The best agreement between calculated and measured peaks was achieved for \(\rho(\text{TiO}_2) = 4.23 \, \text{g cm}^{-3}\), \(\rho(\text{SiO}_2) = 2.53 \, \text{g cm}^{-3}\) and \(\rho(\text{Si}) = 2.33 \, \text{g cm}^{-3}\), which are very close to the bulk values. \(A_{\text{exp}}(\theta)\) was taken as a sum of intensities of HXPES peaks (7) normalized to its constants \(\sigma\), \(c\), \(\lambda\), and \(\gamma\); this parameter was also fitted for each emission angle.

The intensities of the HXPES peaks measured at different emission angles were used to calculate the thickness \(d\) of each layer. These values were then adjusted to give a minimal difference between the experimental and calculated peak intensities at different emission angles. According to the calculations, sample 1 could be represented as a TiO\(_2\)(10.1 nm)/SiO\(_2\)(2.3 nm)/Si structure. The experimental and calculated HXPES peak intensities at different emission angles are shown in figure 13.

According to the HXPES analysis, sample 2 has a more complex structure than sample 1; it can be represented as a three-layer stack TiO\(_2\)/SiO\(_2\)/Si, where the TiO\(_2\) layer is a mix of titanium oxides and metallic titanium, or as a five-layer stack TiO\(_2\)/TiO\(_2\)/Ti/SiO\(_2\)/Si. The calculations of the layer thicknesses were carried out for both models.

In the three-layer model, the sum of all the Ti\(_{2p}\) doublet peaks (from Ti\(^{3+}\) to Ti\(^0\)) corresponds to the TiO\(_2\) layer. Ti\(^{4+}\)\(_{2p}\) peaks correspond to the SiO\(_2\) layer and Si\(^{0}\)\(_{2p}\) peaks correspond to the Si substrate. Following the procedure described above for sample 1, it was established that sample 2 can be considered as a TiO\(_2\)(13.3 nm)/SiO\(_2\)(0.5 nm)/Si stack. The best fit of the experimental data was obtained with \(\rho(\text{TiO}_2) = 4.33 \, \text{g cm}^{-3}\), \(\rho(\text{SiO}_2) = 2.53 \, \text{g cm}^{-3}\) and \(\rho(\text{Si}) = 2.33 \, \text{g cm}^{-3}\). The experimental and calculated HXPES peak intensities at different emission angles are shown in figure 14(a).

In the five-layer model, the Ti\(^{4+}\)\(_{2p}\) doublet peaks correspond to the TiO\(_2\) layer, the sum of Ti\(^{3+}\)\(_{2p}\), Ti\(^{3+}\)\(_{2p}\) and Ti\(^{4+}\)\(_{2p}\) peaks to the TiO\(_2\) layer, Ti\(^{2p}\) peaks to Ti, Si\(^{4+}\)\(_{2p}\) peaks to the SiO\(_2\) layer and Si\(^{0}\)\(_{2p}\) peaks to the Si substrate. Sample 2 was approximated as a TiO\(_2\)(3.6 nm)/TiO\(_2\)(4.4 nm)/Ti(5.8 nm)/SiO\(_2\)(0.5 nm)/Si stack with the density values \(\rho(\text{TiO}_2) = 4.23 \, \text{g cm}^{-3}\).
Figure 14. Experimental (dots) and calculated (lines) values of HXPES peak intensity using the three-layer (a) and five-layer (b) models for sample 2 (3010 eV excitation). For clarity, all the intensities are normalized by the constants $\sigma$, $\iota$, $\lambda$, $\gamma$ and $A_{\text{exp}}(\theta)$.

Figure 15. HRTEM images of samples 1(a) and 2(b).

$\rho(\text{TiO}_x) = 4.33 \text{ g cm}^{-3}$, $\rho(\text{Ti}) = 4.5 \text{ g cm}^{-3}$, $\rho(\text{SiO}_2) = 2.53 \text{ g cm}^{-3}$ and $\rho(\text{Si}) = 2.33 \text{ g cm}^{-3}$. The experimental and calculated HXPES peak intensities are shown in figure 14(b).

A comparison of the results shows that in the five-layer model, the overall thickness of the top three layers (13.8 nm) is 0.5 nm larger than the total thickness of the top TiO$_x$ layer in the three-layer model. This disagreement most likely originates from the assumption of infinitely sharp surfaces and interfaces.

3.3. TEM measurements

The individual thicknesses of the layers were also determined using HRTEM. The measurements were carried out with a Carl Zeiss Libra 200 FE 200 keV microscope. Figure 15 shows HRTEM images of samples 1 and 2. To reduce possible errors due to width gradients, the microscopic and spectral measurements were conducted on the same sample area. The observations were conducted in a cross-sectional geometry, for which the sample was cleaved into two identical parts, with the cleavage directed through the measurement area. Next, these sections were cemented face to face, and the central part was thinned to less than 100 nm by mechanical grinding and subsequent ion milling.

From figure 15, sample 1 can be presented as TiO$_2$(10.6 nm)/SiO$_2$(2.3 nm)/Si and sample 2 as (TiO$_2$+TiO$_x$+Ti)(13.3 nm)/SiO$_2$(0.5 nm)/Si.

4. Summary

The internal structures of 10-nm-thick Ti and TiO$_2$ films deposited onto SiO$_2$(2 nm)/Si substrates by dc and RF magnetron sputtering, respectively, were studied by SXR, HXPES and HRTEM. Atomic concentration profiles of all the chemical elements composing the samples were reconstructed by analyzing the reflectivity curves measured versus the incidence angle at different SXR photon energies. The approach was based on the general philosophical principle of Ockham’s razor, namely, the number of layers representing the sample was gradually increased until the desired accuracy between the experimental and calculated reflectivity curves is archived. The atomic concentration profiles were then refined applying the concept of maximum entropy.
Chemical analysis of the samples by HXPS was carried out on the basis of the scanning photoelectron emission angle at a fixed photon energy, which allowed us to modify the probing depth. The thicknesses of individual layers were determined from the analysis of peak areas of all the detected core levels.

While the TiO$_2$ sample was uniform along its depth direction, the oxidation of the Ti sample resulted in a complex depth distribution of chemical elements, varying from the TiO$_2$ layer on top to Ti mixed with a small amount of titanium oxide inside the sample. The chemical reaction of Ti with the native oxide on the Si substrate caused the decrease in the SiO$_2$ layer thickness from about 2.3 nm to 0.5–0.6 nm. This fact was confirmed by all the three analysis techniques.

The variation of the chemical composition along the sample depth, thicknesses of individual layers and their densities extracted from SXR reflectivity measurements and HXPS are in close agreement and correlate well with the HRTEM images. Thus, the SXR technique allowed full characterization of the multilayered sample structure including the extension of interlayers.

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