Intermixing and thermal oxidation of ZrO₂ thin films grown on a-Si, SiN and SiO₂ by metallic and oxidic mode magnetron sputtering

R. Coloma Ribera,^{1,a)} R.W.E. van de Kruijs,^{1,b)} J.M. Sturm,¹ A. E. Yakshin,¹ and F. Bijkerk¹

¹Industrial Focus Group XUV Optics, MESA⁺ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.

The initial growth of DC sputtered ZrO₂ on top of a-Si, SiN and SiO₂ layers has been studied by *in vacuo* high-sensitivity low energy ion scattering (HS-LEIS) for two gas deposition conditions with different oxygen content (high-O and low-O conditions). This unique surface sensitive technique allowed the determination of surface composition and thicknesses required to close the ZrO₂ layer on all three substrates for both conditions. The ZrO₂ layer closes similarly on all substrates due to more favorable enthalpies of formation for ZrO₂ and ZrSiO₄, resulting in passivation of the Si from the substrate. However, this layer closes at about half of the thickness (~1.7 nm) for low-O conditions due to less oxidative conditions and less energetic particles arriving at the sample, which leads to less intermixing via silicate formation. In contrast, for high-O conditions, there is more ZrSiO₄ and/or SiO_x formation, giving more intermixing (~3.4 nm). *In vacuo* X-ray photoelectron spectroscopy (XPS) measurements revealed similar stoichiometric ZrO₂ layers deposited by both conditions and, a higher interaction of the ZrO₂ layer with the underlying a-Si for high-O conditions. In addition, oxygen diffusion through low-O ZrO₂ films on a-Si has been investigated by *ex situ* angular-resolved XPS (AR-XPS) of samples annealed in atmospheric oxygen. For temperatures below 400°C, no additional oxidation of the underlying a-Si was observed. This, together with the amorphous nature and smoothness of these samples, makes ZrO₂ a good candidate as oxidation protective layer on top of a-Si.

I. INTRODUCTION

Zirconium oxide thin films (ZrO₂) present several attractive properties including high thermal and chemical stability, high dielectric constant, large band gap, high hardness, and good optical performance in the near UV-Vis regions (high refractive index and low optical loss).^{1,2,3} These properties make ZrO₂ thin films suitable for many applications. For instance, ZrO₂ thin films can be used in optical devices such as UV filters and laser mirrors.^{4,5} Apart from other relevant properties, the low reactivity of ZrO₂ with Si⁶ has made ZrO₂ an alternative high-K material to SiO₂ used as gate dielectric for complementary metal-oxide-semiconductor (CMOS) devices,^{1,7} and as dielectric layer for volatile dynamic random access memories (DRAMs).⁸ This low reactivity of ZrO₂ with Si, together with the fact that Zr forms a very stable and inert oxide to possible external contaminants,^{9,10} have made ZrO₂ also a promising candidate as capping layer for optics designed for extreme ultraviolet lithography (EUVL).^{11,12} In the last three applications, oxygen diffusion towards deeper layers is one of the main threats for their performance. Both gate dielectrics and memory devices are usually fabricated at high temperatures under a strong oxidative environment. In such extreme conditions, the poly-Si

^{a)} Author to whom correspondence should be addressed. Electronic mail: r.colomaribera@utwente.nl

^{b)} Author to whom correspondence should be addressed. Electronic mail: r.w.e.vandekruijs@utwente.nl

plug attached to the high-K dielectric layer is oxidized, resulting in a decrease of the effective dielectric constant.^{1,13} Similarly, EUV light induces the cracking of the water vapor present in the lithography vacuum system, generating aggressive oxygen species.¹⁴ These highly reactive oxygen species lead to oxidation of the Si/Mo multilayer mirror (MLM), causing a reflectance drop.¹⁵ In these three cases, the Si layer underneath should not be directly exposed to an oxidative environment. Thus, the ZrO₂ protective layer should be a stoichiometric, inert and closed layer that does not allow transport of oxygen through it.

Like other metal oxides,^{16,17} ZrO₂ usually crystallizes after a few nanometers of film thickness, allowing O diffusion through grain boundaries in the film.^{1,8} Besides, grain boundaries can cause undesired current leakage, and the formation of anisotropic crystalline phases can lead to non-uniformities in the dielectric constant, affecting the performance of CMOS and DRAM devices.^{18,19} Thus, the dielectric layer thickness of such devices should be reduced to ensure an amorphous structure. Since oxides highly absorb in the EUV range,¹⁵ it is also critical to minimize their layer thickness. For instance, a 3 nm ZrO₂ capping layer can cause more than 1% reflectance loss when applied on a Si-terminated high-reflectance MLM, above the maximum loss permitted for such mirrors.²⁰ For all these reasons, an ultrathin amorphous ZrO₂ layer is necessary for both electronics and optical applications to act as an effective diffusion barrier with good optical response.

To study the growth of such an ultrathin ZrO₂ film, a high surface sensitive technique which allows an accurate investigation of the initial growth stages is needed, including the determination of the thickness where the layer closes with Ångström precision. From all surface analysis techniques, low energy ion scattering (LEIS) is considered to be unique for such studies.²¹ This uniqueness relies on the capacity of LEIS to fully separate the information of the outermost surface atomic layer from the layers below the surface,²² providing an accurate monitoring of the surface composition during growth of a thin film until it closes.²¹ More details about this technique can be found in ref.²³.

ZrO₂ thin films prepared by chemical vapor deposition,^{24,25} pulsed laser deposition,^{26,27} sol-gel processing,^{28,29} electron beam evaporation,^{30,31} and sputtering,^{32,33} have been reported. It is known that film structure and film properties are influenced by both deposition process and deposition parameters. In the case of reactive sputtering, Venkarataj *et al.*³² revealed a strong influence of the O₂ partial pressure on the ZrO₂ deposition process at room temperature. They observed a clear transition from an oxidic sputtering mode (for high oxygen content) to a metallic sputtering mode (for low oxygen content) which resulted into different optical and structural properties of the grown ZrO₂ films. In that study and in the other reported deposition studies, ZrO₂ thin films were grown on either natively-oxidized or HF-cleaned Si(100) substrates. But to the best of our knowledge, there are no growth studies at room temperature reported which investigate the initial growth of thin ZrO₂ films directly on amorphous Si (a-Si). This can be relevant for applications where oxides are deposited on a-Si, such as contact and passivation layers for a-Si solar cells.^{34,35} In the present article, we use *in vacuo* high-sensitivity LEIS (HS-LEIS) to study the initial stages of growth of reactive DC sputtered ZrO₂ thin films on a-Si, reactively sputtered sub-stoichiometric Si nitride (denoted as SiN), and SiO₂ substrate layers for two gas deposition conditions with high and low oxygen content,

representing the two mentioned oxidic and metallic sputtering modes. Apart from a-Si, the other SiN and SiO₂ substrate layers have been selected to study the influence of the Si passivation (by nitridation or oxidation) on the ZrO₂ growth. In addition, *in vacuo* X-ray photoelectron spectroscopy (XPS) is used to determine the ZrO₂ stoichiometry and its initial interaction with the underneath a-Si layer for both deposition conditions. Finally, *ex-situ* angular-resolved XPS (AR-XPS) measurements are performed to investigate the oxygen diffusion response upon thermal oxidation of the ZrO₂/Si system.

II. EXPERIMENTAL

ZrO₂ layers were prepared at room temperature using reactive DC magnetron sputtering from a metallic Zr target in an argon-oxygen atmosphere. Two deposition conditions with different oxygen content were chosen for growing the ZrO₂ layers. One with high oxygen content and another with low oxygen content, representing both oxidic and metallic sputtering modes observed and described earlier in ref.³². For the high oxygen conditions, a 1:1 gas mixture of Ar:O₂ was chosen to achieve oxidic sputtering mode. For the low oxygen conditions, a mixture of 0.66% O₂ in Ar was used, which resulted in metallic sputtering mode, following ref.³². We note that specific conditions may vary from one deposition set-up to another and only act as a guide. However, the optimization of the conditions was not part of this study. For simplicity, ZrO₂ layers deposited with high oxygen content and low oxygen content are referred in the text as high-O ZrO₂ and low-O ZrO₂, respectively.

High-O and low-O ZrO₂ layers with thicknesses ranging from 0 to 4 nm were deposited on top of 5 nm a-Si, 1.5 nm SiN/4 nm a-Si and 1.5 nm SiO₂/4 nm a-Si layers (see layered models in Fig. 1). All layered systems were grown onto natively oxidized super-polished Si substrates in an ultra-high vacuum (UHV) setup with base pressure <2 x 10⁻¹⁰ mbar, and their respective layer thicknesses were monitored using quartz mass balances (QMBs), calibrated by *ex situ* X-ray reflectivity (XRR) using a PANalytical Empyrean X-ray diffractometer (Cu-K α radiation, 0.154 nm)

FIG. 1. (Color online) Layered models for ZrO₂ on (a) a-Si, (b) SiN and (c) SiO₂.

For ZrO₂ thickness calibration, several samples with thicknesses in the range between ~2.0 and 10 nm ZrO₂ were deposited on top of 5 nm a-Si layers onto Si substrates for both deposition conditions. As an example, Fig. 2 shows XRR measurements (stars) from 8.9 nm (a) and 10.0 nm (b) ZrO₂ layers deposited under respectively high-O and low-O conditions, together with GenX³⁶ simulations (solid lines) based on the layered models presented in the insets. The GenX program varied thickness, density and roughness of each of the model layers in order to minimize the differences between model simulations and experimental data.³⁶ The accuracy in determining the deposited ZrO₂ layer thickness and layer density was approximately ± 0.2 nm and ± 0.3 g·cm⁻³, respectively. The calibration of the ZrO₂ thickness

was finally obtained from a plot of the extracted as deposited ZrO_2 thickness (including the ZrO_2 thickness that was used to form ZrSiO_4) as a function of Zr QMB thickness for all investigated thicknesses between ~ 2 and 10 nm.

FIG. 2. (Color online) Experimental (stars) and simulated (solid line) specular XRR data for (a) a 8.9 nm high-O ZrO_2 (7.3 nm Zr on QMBs) and (b) a 10.0 nm low-O ZrO_2 (10.1 nm Zr on QMBs) samples deposited on 5.0 nm a-Si onto Si(100) substrates. Left-bottom (a) and (b) inset shows the layered model used for each simulation. Right-top (a) and (b) inset presents the XRR spectrum in the region close to the critical angle, used to extract the ZrO_2 density.

All a-Si, SiN and SiO_2 layers were deposited at room temperature using typical DC or reactive DC magnetron sputtering from a Si target either in Ar atmosphere (for a-Si), an Ar/ N_2 (5:4) mixture (for SiN), or an Ar/ O_2 (25:4) mixture (for SiO_2). The sputtering process was performed with a constant cathode power of ~ 8 W and a pressure of $\sim 10^{-3}$ mbar. (Detailed conditions can be found in ref.²¹).

In vacuo XPS measurements were performed to determine the stoichiometry of the ZrO_2 layers, and their initial interaction with the underlying a-Si layer for the high-O and low-O conditions. For that, 10 nm- and 1 nm-thick ZrO_2 layers were respectively deposited on top of 5 nm a-Si onto Si substrates for both conditions, transferred under vacuum (2×10^{-10} mbar) to the measurement chamber, and finally analyzed by XPS. The XPS instrument used was a Thermo Theta Probe spectrometer using monochromatic Al-K α radiation ($h\nu = 1486.6$ eV). XPS data was evaluated by means of the Thermo Advantage software,³⁷ using Shirley backgrounds and Gaussian-Lorentzian fitted peaks.³⁸ Scofield sensitivity factors were employed for quantification.³⁹

In vacuo HS-LEIS measurements during high-O and low-O ZrO_2 growth on a-Si, SiN and SiO_2 substrate layers were carried out using an ION-TOF GmbH Qtac¹⁰⁰ HS-LEIS spectrometer with a base pressure of 2×10^{-10} mbar, for thicknesses up to which ZrO_2 formed a closed layer. Detailed information about the setup can be found in ref.²². Deposited samples were transferred under vacuum (2×10^{-10} mbar) to the LEIS analysis chamber. The work pressure in the LEIS analysis chamber was $\sim 2 \times 10^{-8}$ mbar during all measurements, corresponding to He used in the ion gun. Sample transfer and measurement were carried out within <10 min after deposition in order to avoid surface contamination. All LEIS measurements were performed using a He^+ ion beam with an energy of 3 keV and a beam current of 3-5 nA, measured with a Faraday cup. The average ion dose was 2.2×10^{14} He^+

ions/cm², below the “static limit” for 3 keV He⁺ ions which implied that less than 1% of the surface was sputtered away during the LEIS analysis.⁴⁰

Oxygen diffusion through ZrO₂ thin films upon thermal oxidation was investigated by *ex situ* AR-XPS. For that, 2 nm low-O ZrO₂ was deposited on 5 nm a-Si onto Si(100). These low-O conditions for growing ZrO₂ were selected due to the lower interaction of ZrO₂ with a-Si which provided a larger amount of elemental Si and enabled an easier oxidation detection of the underneath a-Si layer. A thickness of 2 nm for the ZrO₂ film was chosen slightly larger (~0.3 nm) than the determined closed layer thickness to ensure complete layer closure for these conditions. Several identical ZrO₂ thin film samples were annealed during 20 min at different temperatures (from as deposited to 600°C) under atmospheric environment in a CARBOLITE Elf laboratory furnace that allowed a homogeneous sample heating. *Ex-situ* AR-XPS measurements were conducted before and after annealing, using the previously mentioned XPS instrument and data analysis. The crystalline structure of both ZrO₂ and a-Si films was also investigated. For that, X-ray diffraction (XRD) patterns of the 2 nm low-O ZrO₂ on 5 nm a-Si samples were recorded using a PANalytical Empyrean X-ray diffractometer (Cu-K α radiation, 0.154 nm). In addition, surface morphologies of the as deposited and annealed samples were analyzed using an *ex situ* BRUKER Dimension Edge atomic force microscope (AFM) equipped with a μ masch Hi’Res-C14 tip, featuring a diamond-like spike (radius <1 nm) on the apex of a Si tip, making it suitable for high-resolution scans of flat samples. The AFM image analysis (morphology, roughness) was performed using the WSxM software package.⁴¹

III. RESULTS AND DISCUSSION

A. ZrO₂ growth on a-Si

Since under-stoichiometric oxides may allow O diffusion through their structure in contrast to stoichiometric oxides,⁴² the ZrO₂ stoichiometry of the produced layers for high-O and low-O conditions is investigated first. For that, 10 nm-thick ZrO₂ layers are deposited for both conditions on 5 nm a-Si onto Si substrates, and *in vacuo* analyzed by XPS (see Zr-3d XPS spectra in Fig. 3). Note that the thickness of the ZrO₂ layer is selected to ensure that only this layer is investigated, since XPS averages the atomic composition and the chemical state of the atoms over the outer 10 to 20 atomic layers,²² corresponding to a depth of ~3 to 6 nm.

FIG. 3. (Color online) Zr-3d XPS spectra for high-O ZrO_2 (a) and low-O ZrO_2 (b). Zr-3d_{3/2} (left) and Zr-3d_{5/2} (right) peaks which correspond to ZrO_2 (red solid lines) and ZrO_x (green solid lines), and the layered models of the deposited structures (insets) are displayed in (a) and (b). Note that no elemental Zr is detected for both deposition conditions, as pointed by the dashed lines.

Most of zirconium is oxidized, forming ZrO_2 and no elemental Zr is detected for both ZrO_2 deposition conditions, as depicted in Fig. 3. There is a small amount of ZrO_x (~3%) for the high-O conditions which is almost not present for low-O conditions. This may be attributed to the fact that for high-O conditions the Zr target is not yet saturated by O_2 in the Ar+ O_2 mixture, since initially the Zr target is only pre-sputtered in Ar, and O_2 is introduced just before (<1 min) the deposition starts. Instead for low-O conditions, the Zr target is already saturated at the beginning of the deposition due to an additional pre-sputtering step of ~5 min in Ar+ O_2 mixture. The different approach in the case of high-O conditions is chosen to limit the influence of oxidation of the a-Si substrate layer and to ensure sufficient cleaning of the Zr target, in view of the lower sputter rate for the oxidic sputtering mode. The stoichiometry of the 10 nm-thick ZrO_2 layers, as determined from the O-1s and Zr-3d peak areas, resulted in stoichiometric ratios (O/Zr) of 1.98 ± 0.03 and 1.99 ± 0.03 for high-O and low-O conditions, respectively, close to bulk ZrO_2 . Note that similar ZrO_2 deposition conditions with high and low oxygen content showed different stoichiometric behavior in ref. (Venkarataj *et al.*³²). There, the ZrO_2 layers produced with low oxygen content (denoted as metallic sputtering mode) were under-stoichiometric and the ZrO_2 layers produced with high oxygen content (denoted as oxidic sputtering mode) were stoichiometric. A very sharp transition was observed between both metallic and oxidic sputtering modes,³² and it is possible that our low-O ZrO_2 deposition conditions are just in that transition region.

To confirm that low-O ZrO_2 conditions are in the transition region, we compare the mass density of our 10 nm-thick ZrO_2 layers grown by our two deposition conditions to the average mass density of the ZrO_2 layers produced by the two modes observed in ref.³². Mass densities of our layers are determined by XRR using the layered models depicted in Fig. 2, according to the procedure described in Sec. II. The high sensitivity of the XRR analysis to the ZrO_2 density comes from the critical angle, which is related to the average electron (proportional to mass) density of the layered structure, as well as the amplitude of the oscillations, which is related to the optical contrast between ZrO_2 and the Si substrate, which also strongly depends on the mass density of the ZrO_2 layer. Mass density values of 5.1 ± 0.3 and $5.7 \pm 0.3 \text{ g}\cdot\text{cm}^{-3}$ are obtained for our high-O and low O ZrO_2 layers (see Figs. 2(a) and 2(b), respectively).

In the study carried out in ref.³², average mass density values of 6.5 and $5.2 \text{ g}\cdot\text{cm}^{-3}$ were determined for the ZrO_2 layers deposited by the metallic and the oxidic sputtering modes, respectively. The density of the high-O ($5.1 \pm 0.3 \text{ g}\cdot\text{cm}^{-3}$) and the oxidic ZrO_2 layers ($5.2 \text{ g}\cdot\text{cm}^{-3}$) is similar, denoting comparable conditions. Contrarily, the density of the low-O ZrO_2 layers ($5.7 \pm 0.3 \text{ g}\cdot\text{cm}^{-3}$) is lower (~12%) than the density of the metallic ZrO_2 layers ($6.5 \pm 0.3 \text{ g}\cdot\text{cm}^{-3}$). Specifically, the low-O ZrO_2 density is between the metallic mode density, close to bulk Zr ($6.52 \text{ g}\cdot\text{cm}^{-3}$)⁹, and the oxidic mode density ($5.2 \text{ g}\cdot\text{cm}^{-3}$)³² and exhibits a value close to bulk ZrO_2 ($5.68 \text{ g}\cdot\text{cm}^{-3}$).⁹ This confirms our suggestion that low-O ZrO_2 deposition conditions are

just in the transition region between the metallic and the oxidic sputtering modes, representing a semi-metallic sputtering mode. In addition, based on the previous analysis, high-O ZrO₂ deposition conditions correspond to an oxidic sputtering mode.

Apart from the stoichiometry, it is also interesting to study the initial gas vapor-solid reaction between the sputtered ZrO₂ and the underlying a-Si layer for high-O and low-O deposition conditions. For that, 1 nm-thick ZrO₂ layers are grown on 5 nm a-Si, and also measured by *in vacuo* XPS (see Si-2p XPS spectra for both conditions in Fig. 4). Note that the ZrO₂ thickness is selected in this case to study the full ZrO₂/Si interface (including both ZrO₂ and a-Si layers), since the maximum XPS information depth is about 6 nm.²²

FIG. 4. (Color online) Si-2p XPS spectra for high-O ZrO₂ (a) and low-O ZrO₂ (b). Elemental Si is fitted with a doublet (right, red peaks), while ZrSiO₄ and/or SiO_x species are fitted with a single peak for simplicity (left, green peaks). Layered models of the deposited structures are shown in insets. Note that no SiO₂ peaks are detected, especially for the low-O ZrO₂ conditions, where only ZrSiO₄ is observed, as pointed by the dashed lines.

ZrO₂ deposition produces a clear peak at about 102 eV corresponding to silicate (ZrSiO₄) formation, and no clear stoichiometric SiO₂ peak is observed (~103.5 eV) for both ZrO₂ growth conditions (see Si-2p XPS peaks in Fig. 4). This is in line with other studies where only ZrSiO₄ formation, rather than SiO₂, was observed upon initial ZrO₂ deposition on SiO₂/Si substrates.^{43,44} It should be noted that before ZrO₂ deposition, our 5 nm a-Si layers are slightly oxidized due to pre-sputtering of the Zr target in Ar+O₂ atmosphere, even though the target shutter is closed during this period. This means that our ZrO₂ deposition process is performed on an oxidized Si surface with a similar behavior as the mentioned studies on SiO₂/Si substrates. From the potential chemical reactions at the ZrO₂/Si interface, the ones leading to ZrSiO₄ are thermodynamically more favorable (at least by a factor of 10) than the ones leading to SiO₂.⁴³ Thus, ZrSiO₄ formation would be preferred over SiO₂ formation. Although some of the potential reactions also show ZrSi_x products,⁴³ the presence of oxygen would reduce their formation, favoring oxidized species such as ZrSiO₄.

For high-O ZrO₂ conditions, most of ZrO₂ interacts with the underneath a-Si, forming ZrSiO₄ (see the large ZrSiO₄ peak compared to the elemental Si peak in Fig. 4(a)). This strong interaction may go beyond the silicate and some sub-stoichiometric Si oxide (SiO_x) may be formed, as shown by the small shift (~0.3 eV) towards higher energies of the ZrSiO₄ peak in Fig. 4(a). This shift can also be associated to the formation of a silicate rich in SiO₂, as observed

by XPS in pseudobinary $(\text{ZrO}_2)_x(\text{SiO}_2)_{1-x}$ alloys with increased SiO_2 content.⁴⁵ In contrast for low-O ZrO_2 conditions, only a small amount of a-Si (~22%) reacts with ZrO_2 to form some interfacial ZrSiO_4 , and no apparent SiO_x or SiO_2 -rich silicate is detected (see the small ZrSiO_4 peak appearing at 102.0 ± 0.1 eV in Fig. 4(b)). The large difference between high-O and low-O conditions can be attributed to the different amount of energetic oxygen particles impacting on the sample, resulting in more intermixing (silicate formation) for the high-O conditions.

We now study the initial growth of ZrO_2 on a-Si, including the determination of the thickness when the ZrO_2 layer closes for both conditions. We define a layer of one or more elements to be closed when its surface only contains these elements and other elements from the underneath layer are no longer present on this surface. Our LEIS tool exhibits a high sensitivity to the surface elements which enables a compositional analysis of the outermost atomic layer. This composition can be determined by the surface peaks of the elements present on the surface.²³

LEIS spectra of the deposited ZrO_2 layers on a-Si for high-O and low-O conditions are presented in Figs. 5(a) and 5(b), respectively. For both conditions, the Zr and O surface peaks increase, while Si decreases during ZrO_2 growth (Figs. 5(a) and 5(b)). For high-O conditions, the Si surface peak vanishes at about 3.4 nm ZrO_2 , just when the Zr surface peak saturates (see Fig. 5(a)). This means that about 3.4 nm ZrO_2 are needed to close the ZrO_2 layer on a-Si. This large amount of material required for forming a closed layer can be related to stronger intermixing by ZrSiO_4 and/or SiO_x formation for these conditions, as also observed by XPS (see Fig. 4). In contrast, for low-O conditions, the Si surface peak fully disappears at about 1.7 nm ZrO_2 , at the point when the Zr surface peak reaches saturation (Fig. 5(b)). Due to the minor interfacial silicate produced, the ZrO_2 layer closes at half of the thickness for these conditions.

For high-O conditions, the O surface peak quickly saturates (~0.3 nm ZrO_2) and stays constant due to the strong initial oxidation of the full Si surface and immediate ZrSiO_4 formation just when the target shutter opens (see Fig. 5(a)). Instead for low-O conditions, the O surface peak slowly increases and at the end saturates during ZrO_2 deposition due to less amount of oxygen energetic particles present, which initially leads to partial surface oxidation and sub-stoichiometric silicate formation (see Fig. 5(b)). This initial difference in surface oxidation also results in a different intensity of the Si sub-surface signal (low energy “tail” to the Si surface peak), which arises due to reionization of He^0 that backscatters on Si atoms below the surface.²³ For high-O conditions, the oxygen surface concentration is directly saturated for 0.3 nm deposited ZrO_2 (Fig. 5(a)). The presence of electronegative O species results in an enhanced reionization probability, thereby increasing the tail signal of Si compared to the bare a-Si substrate layer. Since for low-O conditions the surface concentration of oxygen only saturates gradually with increasing ZrO_2 thickness, the height of the Si sub-surface signal increases up to about 1 nm deposited ZrO_2 (Fig. 5(b)).

FIG. 5. (Color online) LEIS spectra of 0.3 to 3.4 nm high-O (a) and 0.3 to 1.7 nm low-O (b) ZrO_2 layers grown on 5 nm a-Si onto Si(100) substrate (solid lines). The magnified view of the Si peak and the layered model of the deposited structure are presented in the respective right-top and left-bottom insets in (a) and (b). 5 nm a-Si spectra are displayed by dashed lines in (a) and (b).

It should be noted here that LEIS cannot discriminate between intermixing by ZrSiO_4 formation and 3D island growth. Both intermixing and 3D island formation would give similar LEIS spectra, leading to a wrong interpretation of our results. Hence, surface morphologies of our grown samples on a-Si for several ZrO_2 thicknesses and for both deposition conditions are investigated by AFM. As an example, AFM images of samples with intermediate thicknesses to close the ZrO_2 layer on a-Si of 1.0 nm (for high-O) and 0.9 nm (for low-O) conditions are presented in Figs. 6(a) and 6(b), respectively. Both samples are flat (see Fig. 6), without observed apparent surface morphology changes relative to the initial Si wafer. The high-O ZrO_2 sample exhibits a root mean square (RMS) roughness value of 0.18 ± 0.05 , and a value of 0.17 ± 0.05 nm is obtained for the low-O ZrO_2 sample. These values and the ones obtained for all other thicknesses are similar to the bare Si(100) substrate, which exhibits an average RMS roughness of 0.20 ± 0.05 nm. As a result, we can exclude the formation of 3D islands as decisive process for layer closure in ZrO_2 growth, which seems dominated by intermixing.

FIG. 6. (Color online) AFM images ($1 \times 1 \mu\text{m}$) of samples with intermediate thickness of ZrO_2 (no closed layer) on a-Si for high-O (a) and low-O (b) conditions. Layered models of the deposited structures are shown in insets.

The intensities of the Zr, Si and O surface peaks presented in Fig. 5 are proportional to the surface concentration (or coverage) of the corresponding element.²² In the determination of such surface coverage, we use the surface peak area, which provides more accurate results for the following quantitative surface composition analysis.²³ The reference peak areas for Zr and Si are directly obtained from 10 nm-thick Zr (free of oxygen) and a-Si deposited samples *in*

vacuo measured by LEIS. The obtained reference values for Zr and Si are $(18.2 \pm 0.9) \times 10^3$ and $(4.0 \pm 0.1) \times 10^3$ counts·nC⁻¹, respectively. Since pure references for O do not exist in literature due to the experimental difficulties of directly measuring solid oxygen, an indirect method to obtain this O reference peak area will be discussed later. The surface atomic density N_i^{ref} of an element i in a reference sample (compound or element) with known mass density ρ , can be estimated by

$$N_i^{ref} \approx \left(\frac{n_i \rho N_{AV}}{M} \right)^{2/3}, \quad (1)$$

where n_i is the stoichiometric number of the element i in the compound ($n_i=1$ for a single element), M is the molar mass of the compound (or element), and N_{AV} is Avogadro's number.⁴⁶ Mass density values of 5.1 ± 0.3 , 5.7 ± 0.3 and 2.3 ± 0.3 g·cm⁻³ are determined from the respective fits to the XRR data of 10 nm-thick high-O ZrO₂, low-O ZrO₂ and a-Si deposited samples, following the method described in Sec. II. The surface atomic densities N_i^{ref} of Zr, Si and O atoms in either high-O ZrO₂, low-O ZrO₂ or a-Si samples are then calculated using the obtained mass density values ρ according to Eq. 1. The surface coverage C_i^{surf} for an element i , expressed as surface atomic fraction, can be determined as

$$C_i^{surf} = \left[\sum_{j=1}^{j_{max}} \frac{S_j S_i^{ref} N_j^{ref}}{S_i S_j^{ref} N_i^{ref}} \right]^{-1} \quad (2)$$

where S_j are the surface peak areas, S_i^{ref} are the reference peak areas, and N_j^{ref} are the surface atomic densities for the different surface elements (from $j=1$ to j_{max}). Using Eq. 2, all surface coverages (Zr, Si and O) for high-O and low-O ZrO₂ layers grown on a-Si are finally obtained, and are displayed in Fig. 7(a) and Fig. 7(b), respectively. It should be noted that this equation can only be applied under absence of matrix effects.²³ If there are no matrix effects, when the Zr LEIS signal is plotted against the Si LEIS signal for different amounts of deposited ZrO₂ on Si, a linear relationship should follow. This has already been observed for the ZrO₂/Si system,²⁴ and was confirmed for the Zr vs. Si peak area in this work (not shown). Thus, matrix effects seem not to be present for our system, and Eq. 2 can successfully be applied. However, to apply Eq. 2 for obtaining the surface coverages, the O reference peak area is still required. To obtain this reference, we know that for each deposited amount of ZrO₂, the surface Vegard's law must be fulfilled

$$\sum_{j=1}^{j_{max}} C_j^{surf} = 1. \quad (3)$$

First, we assume an initial value for the O reference peak area. Then, we use this value to calculate all surface coverages by means of Eq. 2 for each deposited amount of ZrO₂. This value is changed recursively until Eq. 3 is valid for all deposited thicknesses. The obtained O reference peak area for both ZrO₂ conditions is 1170 ± 70 counts·nC⁻¹, similar as the 1180 ± 83

counts·nC⁻¹ reference value reported for O in SiO₂,²¹ demonstrating the reliability of this method.

FIG. 7. (Color online) Zr (squares), Si (triangles) and O (circles) surface coverages for high-O (a) and low-O (b) ZrO₂ layers grown on 5 nm a-Si on Si(100) substrate. The dashed lines through the data points are guides for the eye. The two horizontal dashed lines and the vertical dashed-dot line in (a) and (b) represent the respective limits for the surface coverage (from 0 to 1) and the thickness to close the ZrO₂ layer on a-Si for each conditions.

A similar trend in surface Zr coverage increase with increasing deposited amount of ZrO₂ is observed for high-O and low-O ZrO₂ conditions, as depicted by squares in Figs. 7(a) and 7(b), respectively. Although for low-O conditions, the layer closes at half of the thickness required for high-O conditions due to less intermixing, this similar trend denotes that a similar error function like Zr depth profile develops with increasing ZrO₂ thickness for both conditions, though with different interface width, as explained in more detail in ref.²¹. In contrast, there is a faster decrease of Si coverage that goes in parallel with a quicker saturation of the O coverage for high-O conditions when compared to low-O conditions, as represented by respective triangles and circles in Figs. 7(a) and 7(b). This means that for high-O conditions there is a strong initial oxidation which leads to instant ZrSiO₄ formation just when the deposition starts, as shown by the saturated O coverage at 0.2 nm ZrO₂ (Fig. 7(a), circles). Instead, for low-O conditions there are not enough O energetic particles at these initial stages to produce stoichiometric ZrSiO₄. Thus, an under-stoichiometric oxygen-poor silicate is formed at the beginning. And only after 0.7 nm ZrO₂, the O coverage saturates and fully stoichiometric ZrSiO₄ can finally be achieved (Fig. 7(b), circles).

It is known that Si surface segregation can influence the growth causing additional intermixing, as observed by several systems deposited by room-temperature magnetron sputtering.^{21,48} Apart from silicate and/or oxide formation, we need to study the Si surface segregation effect in order to check its contribution to the overall intermixing process during ZrO₂ growth for both deposition conditions. We can qualitatively study this effect by looking at the in-depth Zr signal (“tail” to the Zr peak) in the LEIS spectra while comparing to the Si surface signal. If there is Si surface segregation, the in-depth Zr signal just below the surface will appear already saturated for a ZrO₂ deposited thickness below the closing of the layer, while the Si surface peak is still visible. Fig. 8 shows the LEIS spectra of high-O (a) and low-O (b) ZrO₂ layers on a-Si for different thicknesses near to the closing of the layer, in order to compare in-depth Zr and surface Si signals.

FIG. 8. (Color online) LEIS spectra of high-O (a) and low-O (b) ZrO_2 on a-Si for different thicknesses near to the closing of the layer. Top-middle insets in (a) and (b) represent the layered models of the deposited structures. Note that the saturation level of the in-depth Zr (“tails”) signal is achieved by the formation of a plateau close to the Zr surface peak.

For high-O conditions, the in-depth Zr signal reaches the saturation level at about 2.9 nm ZrO_2 thickness by the formation of a plateau close to the Zr peak in the LEIS spectrum while there is still a Si surface peak (Fig. 8(a), black spectrum). This means that there is surface segregation of Si for these conditions and suggests that around 2.9 nm the grown ZrO_2 layer is almost a bulk closed layer. At this point, the Si surface coverage is $2.9 \pm 0.5\%$ (from Fig. 7(a), triangles), which can be mostly attributed to the amount of Si segregated towards the surface from the ZrO_2/Si interface. The formed plateau remains for ZrO_2 thicknesses larger than 2.9 nm while the Si segregation effect reduces with increasing ZrO_2 thickness and disappears totally when the layer closes at about 3.4 nm ZrO_2 , as observed by the decrease and the vanishing of the Si surface peak in Fig. 8(a). The Si segregation effect detected for these high-O ZrO_2 deposition conditions may be related to the large amount of O energetic particles impacting the sample that can displace and enhance the diffusivity of interfacial Si atoms. And although ZrSiO_4 formation is the most favorable process occurring at the ZrO_2/Si interface,⁴³ a small amount of unbound Si atoms from this interface can segregate upwards and form surface silicate. This process might be motivated by the minimization of the surface free energy by having Si on the top rather than Zr.⁴⁹

For low-O conditions, there is no evidence of Si surface segregation since the in-depth Zr (“tails”) signal saturates just at the moment when the Si surface peak completely disappears at about 1.7 nm and the ZrO_2 layer closes (Fig. 8(b), red spectrum). The absence of Si surface segregation for this low-O conditions might be due to the small amount of O energetic species impinging the sample which only allow interfacial silicate formation during growth. And as soon as this interfacial zone arrives to its end, the layer closes without surface segregation effects which could lead to additional intermixing.

B. Effect of Si passivation on ZrO_2 growth

We now study the passivation effect of the a-Si layer (by nitridation or oxidation) on the initial growth of ZrO_2 for the two high-O and low-O deposition conditions described in Sec. IIIA. To study that, ZrO_2 thin films have been grown onto SiN and SiO_2 substrate layers,

and *in vacuo* analyzed by LEIS (see layered models of the deposited structures in Figs. 1(b), and 1(c), respectively). The thickness to close the ZrO₂ layer has also been determined for both substrate layers and both deposition conditions. All surface coverages (Zr, Si, O, N) have been extracted from the surface peak areas according to Eq. 2, following a similar procedure as the one discussed in Sec. IIIA for ZrO₂ on a-Si, with minor modifications for the growth on SiN and on SiO₂ layers. For ZrO₂ on SiN, the used surface atomic densities for Si and N atoms are calculated by Eq. 1, using a mass density of $3.6 \pm 0.3 \text{ g} \cdot \text{cm}^{-3}$, obtained from the XRR fit to a 10-nm thick SiN deposited sample, following the method described in Sec. II. Since there are no available references for N, the N reference peak area is determined following the same method used for O in Sec. IIIA, where the surface Vegard's law must be satisfied for all deposited thicknesses (Eq. 3). A reference value for N of $330 \pm 23 \text{ counts} \cdot \text{nC}^{-1}$ is obtained, assuming the same reference value for O of $1170 \pm 70 \text{ counts} \cdot \text{nC}^{-1}$ extracted previously for the ZrO₂ on a-Si system. For ZrO₂ on SiO₂, the used Si surface atomic density is calculated by Eq. 1, by means of a mass density of $2.4 \pm 0.3 \text{ g} \cdot \text{cm}^{-3}$, obtained from the XRR fit to a 10-nm thick SiO₂ deposited sample (see method in Sec. II.). Fig. 9 shows the evolution of the Si surface coverage for ZrO₂ grown on a-Si (squares), SiN (triangles) and SiO₂ (circles) for high-O (a) and low-O (b) conditions. Note that the ZrO₂ thicknesses displayed in Fig. 9 are ranging from 0 nm until the thickness when the ZrO₂ layer closes for each system.

FIG. 9. (Color online) Si surface coverage as a function of deposited amount for ZrO₂ grown on a-Si (squares), SiN (triangles) and SiO₂ (circles) for high-O (a) and low-O (b) deposition conditions. The dashed lines through the data points are guides for the eye. The two horizontal dashed in (a) and (b) represent the respective limits for the Si surface coverage (from 0 to 1). The three vertical dashed-dot lines in (a) and (b) denote the thickness when ZrO₂ becomes a closed layer on a-Si (blue), SiN (red) and SiO₂ (black).

Not considering the initial point at 0 nm deposited ZrO₂, a similar reduction of Si surface coverage with increasing deposited amount of ZrO₂ on a-Si, SiN and SiO₂ substrate layers is observed for high-O conditions (Fig. 9(a)). Instead, for low-O conditions there is an initial difference in decrease of Si surface coverage between different substrate layers for ZrO₂ thicknesses below ~0.7 nm (Fig. 9(b)). This could be attributed to the strong initial oxidation for high-O conditions which leads to a quick stoichiometric ZrSiO₄ formation. Although for low-O conditions, a sub-stoichiometric silicate might be formed at the beginning due to lower amount of oxygen energetic particles, requiring more ZrO₂ to achieve the full ZrSiO₄ stoichiometry. Note that the different initial decrease of the Si surface coverage observed for

low-O conditions on the different substrate layers scales with the Si concentration already present on the surface of either a-Si, SiN and SiO₂, but does not mean that a different sub-stoichiometric silicate is initially formed for each substrate layer.

For high-O conditions, ZrO₂ closes between 3.2 and 3.4 nm, and for low-O conditions, ZrO₂ closes between 1.7 and 1.9 nm on a-Si, SiN and SiO₂, as pointed out by the dashed-dot lines in Figs. 9(a) and 9(b), respectively. Although there is a large difference (by a factor of ~2) between conditions based on the thickness required to close the ZrO₂ layer, there is no apparent effect of Si passivation (by nitridation or oxidation) on the growth of ZrO₂, since the ZrO₂ layer closes similarly on top of all three substrate layers for each conditions. One possible explanation to this behavior might be related to thermodynamics. The enthalpies of formation of ZrO₂ and specially ZrSiO₄ compounds present more negative values when compared to ZrSi₂, Si₃N₄ and SiO₂ compounds (see Table I). Since all competing reactions of formation are exothermic, more negative values denote more compound stability. Thus, the ZrO₂ growth would not be influenced by having either bare Si (a-Si) or passivated Si (SiN or SiO₂) as substrate layers, and ZrSiO₄ and/or ZrO₂ formation would be the dominant processes.

TABLE I. Standard molar enthalpies of formation $\Delta_f H^\circ$ at 25°C in kJ·mol⁻¹ for ZrSi₂, Si₃N₄, SiO₂, ZrO₂ and ZrSiO₄ compounds.

Compound	$\Delta_f H^\circ$	Ref.
ZrSi ₂ (crys.)	-159.4	⁵⁰
Si ₃ N ₄ (crys.)	-743.5	⁹
SiO ₂ (α -quarz)	-910.7	⁹
ZrO ₂ (crys.)	-1100.6	⁹
ZrSiO ₄ (crys.)	-2033.4	⁹

C. Oxygen diffusion response upon thermal oxidation of the ZrO₂/Si system

To study oxygen diffusion through ZrO₂ upon thermal oxidation, the ZrO₂/Si system with minor ZrO₂ interaction with the underlying a-Si layer already from as deposited is considered. The earlier *in vacuo* XPS studies (from Sec. IIIA) reveal less Si interaction with the low-O ZrO₂ layer. Since only a small amount of Si reacts to form interfacial silicate for such low-O conditions, there is still significant unreacted Si that can be used for monitoring the oxygen diffusion process through the initially formed ZrSiO₄ layer. Knowing that 1.7 nm is needed to close the low-O ZrO₂ on a-Si, a thickness of 2 nm is selected for the ZrO₂ layer. Assuming that ~1.7 nm is mainly related to ZrSiO₄, the ~0.3 nm difference corresponds to ZrO₂. Thus, the oxygen diffusion process will not be only through ZrSiO₄ but also through pure ZrO₂. It should be noted that defective oxide structures can lead to enhanced diffusion,⁵¹ therefore structural defects of this ZrO₂ film should be also evaluated when considering the choice of sample conditions for the diffusion studies. We can indirectly evaluate these defects by determining the stoichiometry and the mass density of this ZrO₂ film. Since these parameters for such thin film are difficult to measure experimentally, we consider the parameters from “bulk” ZrO₂ films grown by the two deposition conditions. According to the previous *in vacuo* XPS studies presented in Sec. IIIA for the 10 nm-thick ZrO₂ samples, a similar stoichiometry

close to bulk ZrO_2 is obtained for both conditions, though the high-O conditions present lower density ($\sim 12\%$) than the low-O conditions, that exhibit a density value close to bulk ZrO_2 . This means that the high-O conditions might create a more porous structure with more defects which can lead to higher oxygen diffusion. Hence, apart from the lower reactivity of ZrO_2 with a-Si, this is an additional reason to choose the low-O conditions for the diffusion studies.

Oxygen diffusion through the $\text{ZrO}_2/\text{ZrSiO}_4$ layers is monitored through the increase of the Si-2p XPS peak corresponding to ZrSiO_4 and/or SiO_2 (from now on named Si-2p ox.) and the decrease of the elemental Si-2p peak during thermal oxidation. In addition, the Zr-3d XPS peaks can also be followed to check the impact on both ZrO_2 and ZrSiO_4 formed layers. For such study, 2 nm low-O ZrO_2 samples are grown on 5 nm a-Si layers onto Si substrates, annealed under atmospheric conditions at different temperatures from as deposited to 600°C , and measured by *ex situ* AR-XPS, before and after annealing, to quantify the oxygen diffusion process. Fig. 10 shows the evolution of Zr-3d (a) and Si-2p (b) XPS peaks for several of these samples upon thermal oxidation. Note that the spectra shown in Fig. 10 are normalized to the respective main Zr-3d and elemental Si-2p peaks, after subtraction of a Shirley background.³⁸

FIG. 10. (Color online) Zr-3d (a) and Si-2p (b) XPS peaks for low-O ZrO_2 on a-Si for several samples annealed during 20 min at different temperatures from as deposited to 600°C (solid lines). Bulk Zr, Si, ZrO_2 , SiO_2 and ZrSiO_4 binding energies are marked by dashed lines, and a layered model of the deposited structure is also displayed. Note that the shown spectra are recorded with 34° off normal detection.

As expected, all zirconium is reacted forming ZrO_2 and ZrSiO_4 already from as deposited as observed in Fig. 10(a) (black spectrum) by the absence of Zr elemental (~ 178.9 eV) and the formation of a single Zr-3d_{5/2} peak at ~ 182.0 eV that overlaps with bulk ZrO_2 (~ 182.3 eV). Similar Si-2p peaks are formed for this 2 nm deposited sample and the previous 1 nm deposited sample in Sec. IIIA, as shown by Fig. 10(b) (black spectrum) and Fig. 4(b), respectively. Though, double thickness leads to about the double ($\sim 47\%$) of Si reacting with ZrO_2 at the interface when compared to the previous sample, which is in line with the LEIS results that the interfacial silicate layer still grows up to 1.7 nm deposited thickness. However, it seems that the main product of this interfacial reaction is ZrSiO_4 due to the position of the Si-2p ox. peak centered at bulk ZrSiO_4 (~ 102.0 eV) (Fig. 10(b), black spectrum). Therefore, SiO_2 formation might be negligible upon deposition, and only ZrO_2 and ZrSiO_4 will be formed.

There is a clear shift towards higher energies of the Si-2p ox. peak without increase in its content for the samples annealed at temperatures higher than as deposited until 400°C, as represented by the sample annealed at 350°C (Fig. 10(b), blue spectrum). At the same time, a shift towards higher energies of the Zr-3d peaks is observed (see Fig. 10(a)). This can be attributed to the enrichment of Si in the interfacial ZrSiO₄ layer during annealing without further silicate formation and/or oxidation of the underlying a-Si layer, as confirmed by similar O content from the O-1s peaks (not shown) for the as deposited and annealed samples up to 400°C. Thus, when the temperature increases, Si atoms become more mobile, diffuse up from the a-Si layer and react with the ZrSiO₄ layer, forming a Si-rich silicate. But, within this temperature range, the ZrO₂ and silicate layers block diffusion of oxygen to the underlying a-Si layer. Both energy shifts have also been detected in pseudobinary (ZrO₂)_x(SiO₂)_{1-x} alloys with increased SiO₂ content, corresponding to a Si-rich silicate.^{45,52} These energy shifts can be associated to the less electron-donating nature (i.e., more electronegative) of the second nearest-neighbor Si relative to Zr, when comparing Zr-O-Si and Zr-O-Zr bond arrangements. This decreased electron donation from the second-nearest neighbor slightly decreases the electron density on the metal atom. The resulting more positive electrostatic potential at the Zr atom results in an increased binding energy of the Zr-3d photoelectrons. Similarly, for increasing Si content there will be less electron donation of Zr atoms to Si, leading to an increase of the binding energy of the Si-2p photoelectrons from the Si-2p ox. peak.⁵²

At temperatures above 400°C, the silicate is no longer blocking the diffusion of oxygen and some oxygen penetrates down and oxidizes the a-Si layer forming additional silicate and eventually also SiO₂, as observed by the clear increase and the slight shift to higher energies of the Si-2p ox. peak for the samples annealed at 500 and 600°C (see the respective green and red spectra in Fig. 10(b)). This energy shift detected for the Si-2p ox. peak is even more pronounced for the Zr-3d peaks, denoting enhanced Si diffusion at 500 and 600°C which results in more Si-rich silicate formation (see green and red spectra in Fig. 10(a)). Similar shifts towards higher energies of both Si-2p ox. and Zr-3d peaks have been observed by Hwang *et al.*¹⁹ for thermal oxidized ZrO₂/Si films at temperatures between 400 and 700°C. They also detected a decrease of the elemental Si-2p peak during annealing, which in our case corresponds to the increase of the Si-2p ox. peak relative to the normalized Si-2p peak. In that study, the shift of the Si-2p ox. between 400 and 500°C was associated to either Zr silicate formation (Zr-O-Si bonds) or thermally grown Si sub-oxide (SiO_x, 1 < x < 2). They observed a similar position of the Si-2p ox. peak centered at ~103.5 eV for temperatures between 600 and 700°C. This was related to stoichiometric SiO₂ formation, as also observed in our system at ~600°C (Fig. 10(b), red spectrum).

To quantitatively estimate the oxygen diffusion through the 2 nm low-O ZrO₂ layer deposited on a-Si upon thermal oxidation, the previous AR-XPS data is analyzed in more detail. Note that, as discussed before, the direct oxygen diffusion through ZrO₂ cannot be studied, since there is formation of ZrSiO₄ just when the deposition starts. Thus, oxygen diffusion through the formed ZrO₂/ZrSiO₄ bilayer will be the relevant process, and the thickness evolution of these two layers will be determined for all as deposited and annealed samples.

For quantitative analysis, the Zr-3d and elemental Si-2p peaks are fitted with a doublet. Since the Si-2p ox. peak is rather broad, it is fitted with a single peak for reasons of simplicity. From these fits, only the Zr-3d_{5/2}, Si-2p_{3/2} and Si-2p ox. peaks are considered, and an adapted 2-overlayer model composed by ZrO₂/ZrSiO₄ on top of a-Si substrate is used for AR-XPS quantification (see layered model in Fig. 11). Simplified, this adapted model is based on the Beer-Lambert equation⁵³ and follows a similar method as described by Cumpson and Seah.⁵⁴ Photoelectrons generated at a depth z are attenuated by a factor $e^{\frac{-z}{\lambda \cos \theta}}$, with θ the detection angle and λ the attenuation length. For our specific samples, it has been taken into account that the Zr-3d_{5/2} peak is not only associated to the ZrO₂ layer, but also to the ZrSiO₄ layer. Thus, in our adapted model the Zr-3d_{5/2}/Si-2p ox. and Zr-3d_{5/2}/Si-2p_{3/2} intensity ratios are used to fit the thickness of the ZrO₂ layer, while the ZrSiO₄ thickness is fitted from the ratio Si-2p ox./Si-2p_{3/2}. The attenuation length λ for each XPS peak in each compound (or element) of the layer is calculated according to Cumpson and Seah method⁵⁴ as implemented in the Multi-Overlayer Calculator from Thermo Advantage software³⁷ using bulk mass density values ρ for each overlayer or substrate compound (or element). The bulk intensity ratio R_o of each overlayer compound relative to the substrate is calculated directly as described in ref.⁵⁵. For that, ρ , M and λ for the bulk overlayer and substrate materials are required, where M is the molar mass of the compound (or element) (see all calculated λ and R_o values and all used ρ parameters in Table II).

TABLE II. Adapted 2-overlayer model parameters for AR-XPS quantification of thermal oxidized low-O ZrO₂ on a-Si.

No. L ^a	C ^b	ρ^c	XPS peak	λ^d in ZrO ₂	λ^d in ZrSiO ₄	λ^d in Si	R_o^e
1	ZrO ₂	5.68 ⁹	Zr-3d _{5/2}	1.916	...	...	0.361
2	ZrSiO ₄	4.56 ⁹	Zr-3d _{5/2}	1.916	2.045	...	0.211
			Si-2p ox.	2.007	2.143	...	0.221
Sub	a-Si	2.33 ⁹	Si-2p _{3/2}	2.007	2.144	2.904	...

^aL is the number of the overlayer on the substrate (Sub).

^bC is the chemical formula of each overlayer or substrate compound (or element).

^c ρ is the mass density of each compound (or element) (in g·cm⁻³).

^d λ is the attenuation length of photoelectrons from each XPS peak in each compound (or element) (in nm)

^e R_o is the bulk intensity ratio of each overlayer compound relative to the substrate.

After all input parameters for the model are determined, the two unique free parameters corresponding to the overlayer thicknesses z for the ZrO₂ and ZrSiO₄ layers can be obtained for each temperature. For that, experimental and simulated peak intensity ratios from the three considered XPS peaks (Zr-3d_{5/2}, Si-2p_{3/2} and Si-2p ox.) are calculated for each detection angle and annealing temperature. The overlayer thicknesses z for both overlayers are initially estimated and iteratively changed until the simulated and the experimental peak intensity ratios vs. angle match by a least-squares minimization procedure.⁵⁶ A more detailed information of the method for AR-XPS quantification of multi-overlayer-substrate systems can be found in ref.⁵⁴. Note that for this quantification only a range of detection angles between 34 and 49° off normal is selected, since a wider angular range gives a larger deviation from the model,

probably because the interfaces between layers are not ideally sharp, in line with the nearly 2 nm ZrO₂ needed for forming a closed layer. Fig. 11 shows the obtained ZrSiO₄ (triangles) and the ZrO₂ (circles) overlayer thicknesses for low-O ZrO₂ annealed samples on a-Si at different temperatures between as deposited and 600°C.

FIG. 11. (Color online) Overlayer thickness for ZrSiO₄ (triangles) and ZrO₂ (circles) layers on Si substrate as function of temperature for a 2 nm low-O ZrO₂ sample deposited onto 5 nm a-Si. The dashed lines through the data points are guides for the eye. The adapted 2-overlayer model on a substrate is also shown.

From as deposited until ~400°C, both ZrO₂ and ZrSiO₄ layers present similar overlayer thicknesses, as depicted by circles and triangles in Fig. 11, respectively. Average overlayer thicknesses of 0.8 ± 0.1 and 2.6 ± 0.1 nm are obtained within this temperature range for the respective ZrO₂ and ZrSiO₄ layers. This means that when ~2 nm ZrO₂ are deposited on a-Si, slightly more than half of ZrO₂ (~1.2 nm) reacts with Si (or SiO_x, due to the initial pre-sputtering of Zr in Ar+O₂ mixture) forming ZrSiO₄, and the rest (~0.8 nm) remains as ZrO₂, and no additional oxidation occurs by further ZrSiO₄ and/or SiO₂ formation when the temperature is increased up to ~400°C. Taking into account the molar volumes of ZrSiO₄ and ZrO₂,⁹ and the direct reaction between ZrO₂ and SiO₂ to form ZrSiO₄,⁴³ we can estimate a volumetric molar ratio of ZrSiO₄/ZrO₂ of ~2.0. If we consider that ~1.2 nm ZrO₂ fully reacts with SiO₂, then according to this ratio, about ~2.4 nm ZrSiO₄ will be formed, which almost corresponds to the average ZrSiO₄ overlayer thickness obtained by our 2-overlayer adapted model (2.6 ± 0.1 nm). It should be noted that our 2-overlayer adapted model assumes sharp interfaces between layers, while the LEIS results indicate an error function shaped in-depth concentration profile.²¹ This might lead to certain inaccuracies in the overlayer thickness determination, especially upon annealing.

At temperatures higher than 400°C, there is a slight increase of the ZrSiO₄ overlayer thickness of ~0.3 and ~0.6 nm with respect to the as deposited value (2.6 ± 0.1 nm), as shown in Fig. 11 (triangles) for samples annealed 20 min at 500 and 600°C, respectively. At the same time, there is a small decrease of the ZrO₂ overlayer thickness of ~0.1 and ~0.2 nm compared to the initial value (0.8 ± 0.1) for 500 and 600°C (Fig. 11 (circles)). The decrease of the ZrO₂ thickness is due to the reaction of ZrO₂ with a-Si to form additional ZrSiO₄, which results in an increase of the ZrSiO₄ layer. This also means that the combined ZrO₂ and silicate layer allows oxygen penetration above 400°C, resulting in formation of more ZrSiO₄ and/or SiO₂.

underneath. It should be noted that the shift in binding energy of the Zr-3d peaks upon annealing (see Fig. 10(a)) suggests that all ZrO₂ would be incorporated in a Si-rich silicate, while the AR-XPS model indicates that a slightly decreased pure ZrO₂ top layer is remaining. This could be related to the fact that the model assumes sharp interfaces between layers, while additional intermixing takes place upon annealing. Furthermore, the formation of a more Si-rich silicate just below a sub-nm ZrO₂ surface layer, could also affect the Zr-3d binding energy through change in electronegativity of the next-nearest neighbor atom, as described previously.^{45,52}

There is still a remaining question about the structure of the ZrO₂ and a-Si films from the as deposited and annealed low-O ZrO₂ samples on a-Si, which is supposed to be amorphous. To verify the amorphous nature of both ZrO₂ and a-Si films, XRD measurements (not shown) reveal the presence of an XRD amorphous phase, without appreciable signs of crystallinity, demonstrating the amorphous character of both films in the samples. To confirm this apparent amorphous nature, it is interesting to study the surface topography of these samples. The possible crystallization of the ZrO₂ film upon annealing might lead to an increase of the surface roughness due to growth and aggregation of smaller grains, as observed in several thermal oxidation studies of ZrO₂ films.^{28,29} Therefore, the surface morphology of our samples is analyzed by AFM. As an example, AFM images of an as deposited sample, and samples annealed at 400°C and 500°C are presented in Figs. 12(a), 12(b) and 12(c), respectively.

FIG. 12. (Color online) AFM images (1x1μm) of low-O ZrO₂ on a-Si an as deposited sample (a) and samples annealed during 20 min at 400°C (b) and 500°C (c). Layered models of the deposited structures are shown in insets.

All three as deposited, and annealed samples at 400°C, and at 500°C, exhibit similar flat surfaces (see AFM images in Figs. 12(a), 12(b) and 12(c)), with respective RMS roughness values of 0.22 ± 0.05 , 0.16 ± 0.05 , and 0.16 ± 0.05 nm, close to the uncoated Si(100) substrate and comparable to the intermediate thickness samples presented in Sec. IIIA (see example in Fig. 6(b), for low-O conditions). The small RMS roughness values for all these samples, even reduced for enhanced temperatures due to possible smoothing, confirms the amorphous nature of our ~2.0 nm-thick ZrO₂ films. This smoothing effect has also been observed for thin ZrO₂ samples annealed at 400°C.²⁸ However, in that study, samples were annealed under reduced oxygen pressures ($\sim 10^{-5}$ mbar),²⁸ much lower than in our atmospheric conditions. Still, other annealing studies performed under comparable atmospheric conditions, showed similar surface roughness values (~ 0.2 nm) for temperatures up to 600°C.^{29,57} In these studies, temperatures >600°C provoked surface morphology changes which led to increased RMS

roughness.^{29,57} This was attributed to ZrO₂ crystallization occurring at such enhanced temperatures, which could result into an increase of the oxygen diffusion through the ZrO₂ film due to the appearance of grain boundaries in its just formed polycrystalline structure.^{1,8}

It should be noted that crystallization not only may depend on the annealing temperature, but also on the film thickness. A study performed for ZrO₂ thin films on Si, revealed that ~7 nm films started to crystallize at temperatures between 500 and 600°C, while ~13 nm films started to crystallize at temperatures below 400°C.¹⁹ There, this difference was related to the higher surface/volume ratio of the thinner films that stabilized the amorphous phase for a larger temperature range in order to keep the total Gibbs free energy to the minimum.¹⁹ In our case, the oxygen diffusion process presented previously, which occurs at temperatures >400°C (see Figs. 10 and 11), seems not to be motivated by a crystallization process, due to the apparent amorphous nature of our films up to 600°C. Temperatures higher than this value might be required to crystallize such thin (~2 nm) low-O ZrO₂ films on a-Si, where a large (~2.6 nm) silicate interface is already formed upon deposition (see Fig. 11). Thus, further research is needed to elucidate the nature of this oxygen diffusion process at temperatures >400°C, which leads to more silicate and/or SiO₂ being formed.

IV. CONCLUSIONS

The initial growth of DC sputtered ZrO₂ thin films on amorphous Si has been studied for two sputter gas mixtures with high and low oxygen content (High-O and low-O conditions) by *in vacuo* HS-LEIS. The high surface sensitivity of LEIS makes this technique unique for such studies. Thus, deposited material thicknesses required to close the ZrO₂ layer on a-Si have been determined for both deposition conditions. ZrO₂ forms a closed layer on a-Si at about 3.4 and 1.7 nm for high-O and low-O conditions, respectively. The factor 2 reduction of the thickness to close the layer for the low-O conditions was attributed to the reduction of energetic and oxidative particles arriving at the sample, which leads to minor intermixing by silicate formation. Instead for high-O conditions, not only more silicate and/or even SiO_x was formed, but also ~3% Si segregated up towards the surface from the ZrO₂/a-Si interface, which contributes to additional intermixing.

Furthermore, *in vacuo* XPS has been used to determine the stoichiometry and the initial interaction of ZrO₂ with a-Si for high-O and low-O conditions. Although both conditions produce layers with similar close to bulk ZrO₂ stoichiometry, XRR showed that high-O ZrO₂ layers were ~12% less dense than low-O ZrO₂ layers. Thus, high-O conditions lead to a more porous structure with more defects when compared to the other conditions. ZrSiO₄ formation was the dominant process occurring at the interface for both conditions. However, for high-O conditions, more silicate and/or SiO_x was formed due to the higher flux of (energetic) oxygen particles from the magnetron plasma.

The effect of the passivation of the underlying a-Si layer (by nitridation or oxidation) on the initial growth of ZrO₂ has also been studied. The results showed the absence of such an effect on the ZrO₂ growth, since this layer closes similarly on top of a-Si, SiN and SiO₂ substrate layers. This was attributed to the favorable enthalpies of formation of ZrO₂ and

ZrSiO₄ compounds when compared to the enthalpies of formation of the substrate layer compounds.

Finally, oxygen diffusion through ZrO₂ films under thermal oxidation has been investigated for a 2 nm low-O ZrO₂ film on a-Si by *ex situ* AR-XPS. The results did not show increased silicate and/or SiO₂ formation at temperatures below 400°C, despite the large (~2.6 nm) interfacial silicate formed just upon deposition. At these temperatures, the underlying a-Si was protected against oxidation, with only Si-enrichment of this interfacial silicate being detected. In addition, as deposited and thermally oxidized ZrO₂ samples exhibited an XRD amorphous phase, and presented a low surface roughness, close to the Si substrate. The nature of the oxygen diffusion process for temperatures >400°C could not be associated to crystallization, and more research is needed to understand this process. However, the oxygen diffusion barrier capabilities, together with the amorphous nature and the smoothness of these samples, make ZrO₂ thin films an interesting candidate as oxidation protective capping layers for a-Si and possibly other oxidation sensitive materials.

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