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Initial stages of ZrO_2 chemical vapor deposition on Si(100)-(2 × 1) from zirconium tetra-*tert*-butoxide

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ABSTRACT

The initial stages of chemical vapor deposition of ZrO_2 from zirconium tetra-*tert*-butoxide (ZTB) on Si(100)-(2 × 1) have been studied by scanning tunnelling microscopy (STM) and synchrotron radiation excited photoelectron spectroscopy (PES). The STM images and core level (PES) spectra indicate that the predominant surface modifications induced by ZTB are due to silicon carbonization and formation of zirconium dioxide. The carbonization reaction leads to formation of subsurface carbon and two types of reconstructions are discussed: dimer vacancies and dimer vacancies in conjunction with a rotated surface Si-dimer. Indications for the formation of small amounts of zirconium silicide are also found. No evidence for silicon oxidation can be observed with PES, in contrast to the interface properties previously found after larger exposures to ZTB.

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1. Introduction

Ultrathin films of metal oxides with high dielectric constants have received considerable attention as a replacement to SiO_2 as gate insulator in metal–oxide semiconductors field effect transistor (MOSFET) devices. Zirconium dioxide (ZrO_2) has a high thermal stability, low thermal conductivity and a high dielectric constant, and is therefore a suitable candidate material as gate oxide. MOS devices using ZrO_2 as dielectric have shown most promising electrical characteristics [1,2].

The chemical vapor deposition (CVD) technique is well adapted to gate oxide deposition within a MOSFET manufacturing process. With CVD one can achieve atomic layer control of the film thickness, uniform thickness of large areas, stoichiometric control and excellent conformal step coverage of non-planar devices [3,4]. With a proper choice of precursor it is furthermore possible to grow films at low temperatures with a satisfactory deposition rate, making the method economically viable.

Since the electronic properties of a MOSFET device is strongly dependent on the interfacial properties, studies of the initial stages of film deposition are highly motivated. Moreover, the CVD technique has a very high degree of complexity due to the use of molecular precursors rather than impinging atoms as in physical vapor deposition (PVD) [5–8]. The growth process may involve adsorption, desorption, site-specific reactions and transport of precursor fragments on the substrate surface.

In order to unravel the underlying atomistic processes in CVD of thin films a combination of surface sensitive spectroscopic and microscopic tools is a necessity. We have previously studied CVD growth of ZrO_2 on Si(100) and Si(111) using the zirconium tetra-*tert*-butoxide [$Zr(OC(CH_3)_3)_4$, (ZTB)] precursor [9–11]. The film thickness range in these studies was 4–74 Å. Employing photoelectron spectroscopy (PES) and X-ray absorption spectroscopy (XAS) the interfacial properties and the band alignment were characterized in detail. Growth at 400 °C was found to lead to extensive Si oxidation and hydrocarbon fragments embedded in the interface.

Scanning tunnelling microscopy (STM) is most valuable as it offers the possibility to atomically resolve surface structures at extremely low coverages. There are very few examples of previous investigations of CVD undertaken with STM. From studies of metal deposition using metal carbonyl precursors it can be concluded that STM can reveal significant differences in the CVD growth process as compared to PVD [12,13].

The drawback with STM is however the difficulties in obtaining chemical information. This information can instead be provided by core level photoelectron spectroscopy. The binding energies of the core levels are element specific and detailed information about the



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local chemical surrounding is obtained by the chemical shift. The technique is surface sensitive by nature due to the detection of electrons. By exploiting the virtues of high photon flux and variable photon energy at a synchrotron radiation source the surface sensitivity can be dramatically enhanced as compared to standard XPS instruments. This allows for studies of the very low surface coverages needed in order to understand the initial nucleation processes.

In this paper, we use STM and core level PES to study the initial stages of ZrO_2 chemical vapor deposition on the Si(100)-(2 × 1) surface from the ZTB precursor. We report on the details in the ZTB surface reactions involved in the formation of submonolayer structures. It is possible to identify two principal surface processes: Silicon carbonization and formation of ZrO_2 . We propose that the two types of surface modifications can be distinguished in the STM images. The carbonization process leads to characteristic surface reconstructions, the structures of which are discussed. Indications for Zr–Si bond formation are found but there is no sign of silicon oxidation. The absence of observable Si oxidation makes the initial stages quite different from the latter stages of growth.

2. Experimental

The experiments were performed in two different Ultra High Vacuum (UHV) systems with a base pressure lower than 2×10^{-10} torr, one for each technique used (STM and PES). The STM measurements were performed with a customised variable temperature (VT) UHV scanning probe microscope from Omicron Vakuumphysik GmbH, Germany. All STM data were acquired in the constant current mode at room temperature (RT), and are presented as top view grey scale images with darker colors corresponding to lower levels. Both Pt/Ir and W tips were used for the experiments. Subsequent reconditioning of the tip was undertaken by running line scans at 10 V sample bias and 50 nA tunnelling current. This procedure resulted in stable and reproducible images of the surface. All images shown here correspond to occupied states $(V_t < 0)$, since it was very difficult to probe the unoccupied states after ZTB dosing. The photoelectron spectroscopy (PES) measurements were carried out at beam-line I311 at MAX-lab [14]. The end station is equipped with an electron energy analyzer of type SCIENTA SES200. The spectra are calibrated relative to the Si $2p_{3/}$ $_2$ peak for the clean Si(100)-(2 \times 1) surface, set to 99.2 eV binding energy (BE) relative to the Fermi level.

In both cases, a separate preparation chamber is connected to the analysis chamber, equipped with low energy electron diffraction (LEED) and sample heating facilities, and on which the dosing system was connected. The zirconium tetra-*tert*-butoxide (ZTB) precursor (99.99%, Stream Chemicals) was introduced in a pyrex tube welded to a conflat (CF) flange and swiftly connected via a valve to the dosing system. The later was in its turn connected to the preparation chamber via a precision leak valve. All vacuum parts were thoroughly passivated by exposure to ZTB right after baking.

Small rectangular samples were cut from *n*-doped (P) Si(100) wafers (Polishing Corp. of America, $\pm 0.5^{\circ}$, 0.1-1.0 ohm cm⁻¹). Dust particles were removed by blowing with dry N₂. The samples were put into the UHV systems as received. This was followed by a thorough outgasing/annealing procedure [15], which involved flashes to 1250 °C by passing direct current through the sample. This procedure resulted in clean samples according to PES and STM standards.

It can be noted that the tolerance for misorientation is 0.5° for the present grade of silicon wafer. The misorientation observed on the stepped images obtained on the clean surface is within this value. For different samples cut from approximately the same position of the wafer but rotated 90° relative to each other, the sample steps were also oriented 90°. Hence, the small terraces are not primarily induced by the cleaning procedure but are an inherent property of the wafer.

While heated to 400 °C, the sample was exposed to ZTB via a stainless steel tube (10 mm in diameter). Some relatively thick films were always produced to confirm that the system was working satisfactorily and to further passivate the UHV parts. The doses are given in milliLangmuirs (mL, 1 mL = 10^{-9} Torr s) read as the background pressure.

3. Results

3.1. STM images

A top view of the clean Si(100)-(2 × 1) surface is presented in Fig. 1a. It consists in elongated terraces typically about 20 nm wide and separated by monoatomic steps. No step bunching was observed and the step density is as expected for the specified misorientation of the wafer. Rows of silicon dimers run along the terraces, rotated by 90° from one to another. Two different types of defects are observed in good agreement with previously published data and consist in single dimer vacancy (DV) defects (also denoted type A defects) and half missing dimer defects (type C defects). Their density is also in agreement with the literature, with about 1 A-type defect and 1.2 C-type defect per 5×5 nm² [16,17]. Overview images of at least 100×100 nm² (not showed here) exhibit the same low defect density. The zigzag chains are due to imaging of "frozen" buckled dimers, as observed previously [16].

The image presented in Fig. 1b corresponds to a $20 \times 20 \text{ nm}^2$ topograph obtained after 0.1 mL ZTB exposure. It stands clear that the defects density has increased dramatically already after this small dose. The number of dimer vacancies is considerably higher than before ZTB exposure, with up to 15.5 DV per $5 \times 5 \text{ nm}^2$. At several places adjoining DVs are observed forming one-dimensional "trenches" perpendicular to the dimer rows. Extended grooves along the Si(100) [011] direction are also imaged (labelled E). The depth of these dark areas is about 0.5–1.0 Å. As their length varies, the evaluation of their density is not reported here. Moreover, a small number of very bright protrusions can be observed, typically adjacent to the grooves E. The height of the bright spot from the top of the dimer rows is about 1.5 Å. From the line scan in Fig. 1 it can be inferred that this height is in good agreement with the apparent step height.

Furthermore, an intriguing observation is the appearance of small reconstruction patches (R) randomly across the surface, with a density of about 4 per 5×5 nm². In these patches, one dimer is missing and the other is replaced by a smaller protrusion. These patches thus cover each an area approximately corresponding to a (3×2) cell. The protrusion within the R feature is centered in the direction of the dimer rows and off centered in the direction perpendicular to the dimer rows. In the STM images, the protrusions appear at intermediate height as compared to the bottom of the grooves E and the dimer rows. They are not tip-induced artifacts as their position varies from defect to defect within the same image and are independent of the scanning angle. The vast majority of the defects observed at this stage can be assigned to DV, E and R categories, either separately or in combination. However, the R reconstructions are always observed as separate entities or in combination with E or DV defects, that is, there is no tendency for extended (3×2) island formation.

Fig. 2 shows a $50 \times 50 \text{ nm}^2$ STM topograph after a ZTB exposure of 0.2 mL, i.e. after approximately doubling the exposure. The substrate dimer rows are still visible and the (2 × 1) areas amount to at most 50%. The rest of the surface is basically imaged as depressions running along the [011] and the [011] directions. At this



Fig. 1. Filled states STM topographs for (a) the clean Si(100)-(2 × 1) surface and (b) the surface of the same sample after 0.1 mL of ZTB exposure. The sample was kept at 400 °C during exposure to ZTB. The topographs are measured at room temperature using a W-tip. The sample bias was -1.4 V in both measurements and the tunnelling current was (a) 2.7 nA and (b) 2.0 nA. The image of the clean surface (a) shows a low density of A-type (dimer vacancy, DV) and C-type defects. After exposure (b) an increased amount of dimer vacancies (DVs) are observed, sometimes forming trenches. Additional defects are squares or elongated areas along the S-i(100) high symmetry directions imaged as depressions (E) and small reconstructions (R).

stage, the high defects density precludes a clear separation into the different types previously defined (E, DV, or R). No preferential reactions are observed at the step edge. As seen by comparing Fig. 1b and Fig. 2, the number of very bright 1.5 Å high protrusions has increased considerably although their overall surface coverage remains very small. The majority of these bright protrusions appear as singular entities but there are also a few aggregates.

3.2. Core level photoemission spectra

Core level photoemission spectra are shown in Figs. 3 and 4. In the PES experiments ZTB was dosed in two steps. The first dose



Fig. 2. Filled states STM topographs of a Si(100)- (2×1) surface exposed to 0.2 mL of ZTB at 400 °C. The topograph is measured at room temperature using a Pt/Ir-tip. The sample bias was -1.9 V and the tunnelling current was 0.9 nA. The substrate dimer rows are still visible. No preferential reactions are observed at the step edge. Apart from the significantly increased area of depressions there is also a substantial amount of very bright protrusions.

amounts to a nominal exposure of approximately 0.2 mL. This dosage results in no detectable ZTB-induced Zr 3d, C 1s and O 1s signals. Only very small changes in the Si 2p spectrum were observed. Most apparent was a slight decrease of the state associated with the "up-atoms" of the surface dimers forming the (2×1) reconstruction (spectra not shown).

The total nominal dose after the second exposure is estimated to about 1 mL. Zr 3d, C 1s and O 1s signals are now detectable and the spectra are shown in Fig. 3. The Zr 3d_{5/2} BE of 182.3 eV suggests that Zr⁴⁺ species are present, see Fig. 3a [18]. It is possible also to discern very weak structures at 180-178 eV BE. This is indicative of a minute amount of Zr⁰, most likely due to silicide formation [19]. There is one symmetric O 1s peak at 532 eV BE (Fig. 3b). The C 1s spectrum of the clean surface displayed in Fig. 3c has a broad structure at 284.4 eV BE and a weak feature at 282.8 eV. The peak of 284.4 eV BE is attributed to spurious carbon in graphitic form due to surface contamination. The peak of 282.8 eV BE is assigned to carbidic carbon formed from surface contaminations present during the annealing procedure in the cleaning process. After 1 mL ZTB exposure, the intensity at 282.8 eV, i.e. the signature of carbide-like species, increases significantly, whereas the intensity of the peak due to graphitic carbon is unchanged. Since no additional intensity emerges at 284-285 eV the presence of adsorbed hydrocarbons on the surface can be excluded [10,20]. The behavior at this early stage of film nucleation is thus different from that found for a ZTB-grown film a few Å thick, where clear evidence for hydrocarbon species is found [10]. The formation of carbonaceous residues including C–O bonds is expected to give rise to C 1s states at 286-287 eV [10,20]. The C 1s spectrum does not give any clear evidence for the formation of such species.

To obtain a rough estimate of the oxygen coverage a Si(100) surface was oxidized with O_2 . An assumption was made that the 5 Å thick SiO_x film produced in this way correspond to about 1 mL oxygen. By normalizing the integrated O 1s intensity the O coverage after 1 mL ZTB exposure was estimated to be 0.1–



Fig. 3. Zr 3d (a), O 1s (b) and C 1s (c) core level photoemission spectra before and after exposure to 1 mL of ZTB. The spectra are normalized to number of scans and photon flux.

0.2 mL. The tabulated atomic cross sections [21] suggest that the carbon coverage is of a similar magnitude. That is, the C:O ratio is found to be lower than the factor of four expected from the stoichiometry of the ZTB molecule (16:4). No reliable value of the amount of Zr could be attained.

Si 2p spectra for the clean Si(100)-(2×1) surface and after 1 mL ZTB are shown in Fig. 4a. Two different photon energies were used, 114 eV and 150 eV. These values provide Si 2p spectra with low and high surface sensitivity, respectively [22]. In Fig. 4b the photon energy dependent surface sensitivity has been used to separate the spectra into a "bulk" contribution and a "surface" contribution. This was accomplished by normalizing the two spectra to

the low BE shoulder followed by subtraction. Since the low BE shoulder is associated with surface states the difference spectrum represents the states of bulk character. The comparison at the bottom of Fig. 4b shows that the changes in the bulk contribution upon ZTB exposure are negligible. The surface contribution to the spectrum for the clean (2×1) surface contains several components. In the following only the $2p_{3/2}$ spin-orbit component of the various species will be considered for simplicity and brevity. The structure at 98.6 eV BE (labeled 1) is associated with the "up-atoms" of the surface dimers forming the (2×1) reconstruction [22]. The state at 99.30 eV BE (labeled 2) contains contributions both from the dimer down-atoms and second layer atoms [22,23]. These have not been delineated for clarity.

The exposure to 1 mL ZTB induces changes in the Si 2p surface contribution as shown at the top of Fig. 4b. The relative intensity in the BE regime 98.5–99 eV has decreased significantly and there is no well-resolved structure. The decreased intensity of state 1 upon ZTB exposure can be due to dimer decomposition or saturation of the surface dangling bonds [23]. However, state 1 is not sufficient in order to obtain a good fit in this BE regime – an additional state of 98.9 eV BE is also needed (labeled 3). We attribute the new state to formation of zirconium silicide. ZrSi_x has been found to give rise to a peak at 98.8 eV, well in line with the BE of state 3 [19]. The formation of small amounts of $ZrSi_x$ is consistent with the appearance of weak Zr⁰ states in the Zr 3d spectrum. With respect to the STM images it is furthermore noteworthy that the decrease of state 1 (about 60%) suggest that the situation attained after 1 mL ZTB in the PES system is comparable to the situation attained after 0.2 mL ZTB in the STM system.

From Fig. 4b it is evident that exposure to 1 mL of ZTB also gives rise to a significantly increased relative intensity at about 99.5 eV. Keeping state 2 unchanged in shape and BE position from the spectrum of the clean surface, an additional component located at 99.55 eV (labeled 4) is needed to reproduce the extra intensity. Features at this BE have previously been observed upon reaction with hydrogen and ethylene [23,24]. The deposition temperature is however close to that of hydrogen desorption [24]. That state 4 is the result of the reaction with a carbonaceous compound is more likely. We therefore propose that this state is related to the C 1s peak, which then suggests the formation of a SiC-like compound.

Especially noteworthy is finally that exposure to ZTB does not lead to the formation of oxidized Si species. The Si $2p_{3/2}$ component of Si¹⁺ is located at a BE 0.9–1.0 eV higher than that of the bulk peak and higher oxidation states appear at even higher BE:s. There is no sign of such states in the Si 2p spectrum. Thus, during the initial stages Si react with ZTB by formation of Si–Zr and Si–C bonds.

4. Discussion

The PES results demonstrate that the initial reaction between Si(100)- (2×1) and ZTB at 400 °C leads predominantly to formation of ZrO_2 , $ZrSi_x$ and SiC. The STM images show that the interaction with ZTB gives rise to dark patches following the high symmetry directions, bright protrusions, reconstructions described as (3×2) units and an increased density of dimer vacancies. In the following, we will discuss the relation between the PES results and the STM structures and compare the initial stages of ZTB-mediated ZrO₂ growth with our previous results on the latter stages of the growth.

A patch of ZrO_2 must have a lower density of states than the Si surface within a few eV from the Fermi level and should therefore appear as a darker area in the STM images. The most straightforward explanation is therefore that the dark patches (labelled E in Fig. 1b) are associated with ZrO_2 . Previous STM results for the reaction of O_2 with Si(100)-(2 × 1) at room temperature reveal that



Fig. 4. (a) Si 2p spectra for the Si(100)- (2×1) surface before and after small doses of ZTB. The spectra recorded at two different photon energies, 114 and 150 eV, of which the latter results in a higher surface sensitivity. (b) Separation of the spectra in contributions predominantly from the bulk and surface regions, respectively. The spectra are normalized as to have the same maximum intensity in order to facilitate comparison of relative intensities.

 SiO_x gives rise to dark patches following the high symmetry directions [25–27]. These patches appear as depressions at both positive and negative bias. From this follows, that the ZrO_2 areas are imaged similar to the SiO_x areas.

The oxidation of Si(100) leads furthermore to the appearance of bright protrusions, observed as such at both positive and negative bias [26,27]. The apparent height of the bright protrusions has been reported to be 1.4 Å [27], in good agreement with the 1.5 Å found in the present study. It has been argued that bright sites appear in the STM image due to (neutral) Si atoms ejected to the surface by the oxidation reaction [25]. In an alternative picture based on scanning tunnelling spectroscopy, the bright sites are oxidized Si adjacent to adsorbed oxygen [27]. In our case, the origin of the bright protrusions is even more uncertain since there are several different elements present. The Si 2p spectrum shows however no sign of oxidized Si atoms. Thus, if the bright sites are associated with Si atoms, they are either due to neutral ejected atoms or due to oxidized atoms too few to be observable with PES.

The PES results, and to some extent the STM images, suggest that carbon incorporation is most likely upon small exposures of ZTB at 400 °C. The BE of the C 1s peak is identical to that reported for the $c(4 \times 4)$ structure. The C atoms of the $c(4 \times 4)$ structure are embedded in a subsurface layer as inferred from the BE of the C 1s peak (282.8 eV) [28,29] and X-ray photoelectron diffraction results [30]. Bias-dependent STM images suggest that the carbon atoms are located in the fourth layer [31]. The Si 2p spectrum exhibits a component shifted by +0.45 eV vs. the bulk peak. A similar shift has previously been observed upon annealing of a C₂H₄ layer on Si(100) to a temperature at which the $c(4 \times 4)$ structure is formed [24]. This is another indication that similarities to the $c(4 \times 4)$ structure exist in our case. The C:O atomic ratio is furthermore lower than that of the ZTB molecule. Given the surface sensitivity of the measurements, it is possible that the low C:O ratio reflects different locations of the carbon and oxygen atoms, i.e. the carbon species is located subsurface while the oxygen species is at the surface. The C:O ratio can however also be decreased due to desorption of carbonaceous species (most probably isobutene [32]).

Moreover, the STM image recorded after the lowest ZTB exposure reveals an increased density of DVs by more than one order of magnitude. These DVs are in some cases are forming one-dimensional trenches, as seen in Fig. 1b. A previous STM study supported by *ab initio* calculations of surfaces with low carbon coverage formed by hydrocarbon reactions demonstrate that incorporation of C in the fourth layer is most likely [33]. On top of the carbon atom a surface dimer is missing and the reconstruction is commonly denoted DV41 [33]. From this follows that the ZTB induced behavior observed in Fig. 1b can be interpreted in terms of carbon incorporation and DV41 formation [33].

There is no conclusive result that shows that the R reconstructions are induced by carbon species. However, given the amount of carbon provided by the ZTB molecule this is plausible. A tentative interpretation of the R structure is shown in Fig. 5. A carbon atom has been placed in the fourth layer and the (2×1) dimer above the carbon atom is missing, i.e. a DV41 defect. In addition, a rotated dimer (RD) has been introduced next to the DV41. A DV41+1RD defect is consistent with the STM image of the R feature: the structures are confined within a (3×2) cell and a protrusion that is off-center in the direction along the (2×1) rows can be expected.

The $c(4 \times 4)$ structure has been descried in terms of DV41 + 2RD defects [31]. The model presented in Fig. 5 can in principle be viewed as locally similar to the $c(4 \times 4)$ reconstruction. However, the $c(4 \times 4)$ structure has a strong tendency to grow by island formation, in contrast to the dispersed nature of the R features. Even at an exposure where about half of the surface is affected by ZTB, no sign of $c(4 \times 4)$ patches can be found. The quenching of the c(4 × 4) island formation can be related to the complexity of the ZTB decomposition, which involves both ZrO₂ formation and subsequent reaction with the hydrocarbon groups.

Apart from the formation of ZrO_2 and SiC there are two other observations in the PES spectra that are noteworthy: the absence of oxidized Si and the finding of very small amounts of Zr^0 . The formation of ZrO_2 without oxidation of Si raises the question of how the ZrO_2 is linked to the Si substrate. In the absence of oxidized



Fig. 5. The figure shows a tentative structure model of the R reconstruction observed in the STM image shown in Fig. 2b. The carbon atom is located in the fourth layer, above which a surface dimer is missing. This is denoted a DV41 defect. Adjacent to the DV41 is a rotated dimer (RD). The DV41 + 1RD configuration is confined within a (3×2) cell in line with the STM image.

Si a ZrO₂–Si interface has to contain Zr suboxide species bonded to Si atoms. We have no conclusive evidence for Zr in an intermediate oxidation state, i.e. +1 to +3. However, the Zr 3d BE of an O₃Zr–Si species may be shifted by about –1 eV relative to the Zr⁴⁺ peak assuming a 3+ oxidation state [34]. The Zr 3d peaks shown in Fig. 4a are nearly 2 eV broad and the presence of a Zr³⁺ minority species cannot be excluded. The Zr⁰ species is most likely associated with the formation of ZrSi_x as discussed above. We have however no STM structure that can be identified as due to ZrSi_x and we can therefore not determine whether ZrSi_x is formed separately or e.g. in connection with ZrO₂.

The results discussed above demonstrate a very different behavior at the very beginning of the growth as compared to the later stages of growth. We have previously studied ZTB-mediated ZrO₂ growth in the thickness regime 4–74 Å [10]. Using PES we found that an extended interface of about 30 Å thickness is formed. The interface can be described in terms of a $ZrSi_xO_y$ layer with a composition that varies with the distance from the Si(100) substrate. The Si 2p spectrum for a thick film (51 Å) gives evidence for extensive Si oxidation. A distribution of oxidized species is observed of which the +4 state clearly dominates [10]. The situation is different for thinner films. Fig. 6 shows a Si 2p spectrum for a 4 Å thick film on Si(100). A feature shifted by +0.3 eV relative to the bulk peak is needed to obtain an accurate fit. This is exactly the position previously found for the state labeled 2 in Fig. 4b, which was associated with dimer down-atoms and second layer atoms. Si atoms bonded to hydrocarbon also give rise to a peak at this binding energy [20,24]. Since the 4 Å film contains Si bonded to hydrocarbon fragments a contribution to this state is possible. However, the peak still carries the label 2 for simplicity. Most important is that oxidation of Si is evident after 4 Å deposition but in contrast to the thick film the Si¹⁺ state is predominant. For submonolayer coverage no oxidized Si species is detectable with PES as shown in Fig. 4. Consequently, oxidation of Si starts by formation of Si¹⁺ species.

C 1s states in the BE range 283.6–285.3 eV were also observed for the thicker films [10]. We assigned the state at 283.6 eV to carbidic carbon but in the light of the present findings all the C 1s states observed at film thicknesses of 4–74 Å are rather associated with various forms of surface hydrocarbon fragments. That is, carbon incorporation and formation of a SiC compound is only found at low (submonolayer) coverage.



Fig. 6. The Si 2p spectrum for a 4 Å thick ZrO_2 film deposited on the Si(100)-(2 × 1) surface. The presence of oxidized Si in the form of Si¹⁺ is clearly observed.

In the present case the photon flux was higher than in our previous study [10], which in combination with a much lower coverage may increase the susceptibility towards radiation-induced reactions. We can therefore not completely exclude radiation induced hydrocarbon decomposition and subsequent SiC formation. However, in our previous work we were able to correlate the presence of oxidized Si to the presence of hydrocarbon species [10]. This is the case already after deposition of 4 Å where the Si¹⁺ species is observed (Fig. 6) along with hydrocarbon species [10]. The absence of oxidized Si in the PES spectrum at submonolayer coverage (Fig. 4) is not likely to be an effect of radiation damage. Provided that SiO_x is needed to stabilize adsorbed CH_x the absence of CH_x at submonolayer coverage is fully consistent with the absence of SiO_x.

From this it stands clear that the reactions involving the butoxy ligands and the Si atoms changes drastically somewhere between submonolayer coverage and 4 Å film thickness. Carbon incorporation has to be terminated and replaced by processes that yields surface hydrocarbon fragments and allows for Si oxidation. The

complexity of the surface precludes a more detailed description of the processes.

5. Conclusions

The initial stages of chemical vapor deposition of ZrO_2 from zirconium tetra-*tert*-butoxide (ZTB) on Si(100)-(2 × 1) have been studied by STM and PES. The decomposition of the ZTB molecule leads to carbon incorporation and formation of SiC. It is proposed that dimer vacancy structures and (3 × 2) patches observed with STM are carbon induced. A model consistent with a (3 × 2) structure is presented. Indications for Zr–Si bond formation are found but there is no sign of silicon oxidation.

The results are compared to those previously attained upon deposition of thicker films. The absence of Si oxidation and the SiC formation makes the initial stages quite different from the latter stages of the growth. Between submonolayer coverage and 4 Å film thickness the reactions involving the butoxy ligands and the Si atoms has to change from processes giving rise to carbon incorporation and ZrSi_x to processes leading to surface hydrocarbon fragments and SiO_x.

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