



Chemisorption of *tert*-butanol on Si(100)

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ABSTRACT

The chemisorption of *tert*-butanol, an important product in atomic layer deposition (ALD) of ZrO₂ from the precursor, zirconium tetra-*tert*-butoxide, on Si(100)–(2 × 1), has been investigated using Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD). The main desorption products of the TPD experiments are isobutene and molecular hydrogen. A comparison of TPD results obtained with a clean silicon surface with that from a hydrogen-terminated Si surface indicates no chemisorption in the latter case. AES measurements reveal the presence of carbon on the sample after TPD; the amount of carbon tracks the isobutene yield in TPD experiments. A comparison is made of observations with those expected from the known reactions of simple alcohols on Si(100)–(2 × 1) and the chemisorption attributed dominantly to O–H bond scission to yield an H and *tert*-butoxy-group-terminated surface.

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1. Introduction

Atomic layer deposition, including epitaxy, is an important emerging technology for advanced microdevice fabrication. It offers the advantages of surface conformality, precise layer control, and, in many cases, low deposition temperature [1–6]. The key to these advantages is controlled surface chemistry at the growth interface. In this regard, it is important to choose precursors with the appropriate chemical properties for both layer-by-layer growth and a suitable initiation reaction for the first monolayer. In practical terms, these two requirements mean that surface reactions must be self-terminating for each atomic cycle and that the initial reaction on the substrate surface must yield a full-monolayer of chemisorbed species, which can subsequently react to form one of the steps in the sequential growth process. For example, in the case of Al₂O₃, the precursors are Al(CH₃)₃ as the Al metal source and H₂O as the metal oxidant [2,3,7]. Alternatively in the case of CdS deposition, metal-organic cadmium and H₂S are used [6,8]; in the latter case the evolution of the layer-by-layer chemistry as well as its terminating groups have been determined clearly in ultra high vacuum (UHV) surface studies [6].

One major potential application of ALD is in the deposition of high- κ dielectrics such as HfO₂ and ZrO₂ [1,4,5]. One recent precursor candidate for this application is zirconium tetra-*tert*-butoxide (ZTB), which has a relatively high-vapor pressure at room temper-

ature and is thermally stable to temperatures less than 523 K [4,9]. It is known that ZrO₂ growth is by an ALD-like mechanism, which is sketched schematically in Fig. 1 based on the studies by the George group and the Leskelä group [4,9]. As is shown, the reaction proceeds via a self-limiting reaction of one of the four *tert*-butoxy groups with surface-bound hydroxyl groups, generating *tert*-butanol as a byproduct. This reaction is then followed by exposure of the partially decomposed-precursor-decorated surface to H₂O, thus reacting with the remaining *tert*-butoxy groups to again form a surface terminated with OH groups and prepare the surface for an additional cycle [4].

A crucial question with regard to ZTB, and in fact any organometallic, is its propensity to deposit deleterious carbon at the initial growth interface. In the case of growth on a Si surface, many recent very fundamental UHV studies of Si surface reactivity have shown clearly that this surface is reactive and offers a variety of reaction pathways for molecular adsorbates [10–14]. Obviously carbon may be formed in any of the possible surface decomposition channels of the precursor. However, decomposition of *tert*-butanol ((CH₃)₃COH), after release from the precursor, can also play an unintended role in contributing to surface carbon due to any of its reactions with the surface. Thus while the chemical properties of *tert*-butanol itself are clearly different from *tert*-butoxy groups, the reaction of the *tert*-butanol is important since it is likely present as an impurity when *tert*-butoxy substituted transition metal compounds are used in ALD. In this connection, earlier studies by Kim et al. [15] had indicated a probable route to surface decomposition of *tert*-butanol on Si(100), although the focus in those experiments was considerably different than in our case.

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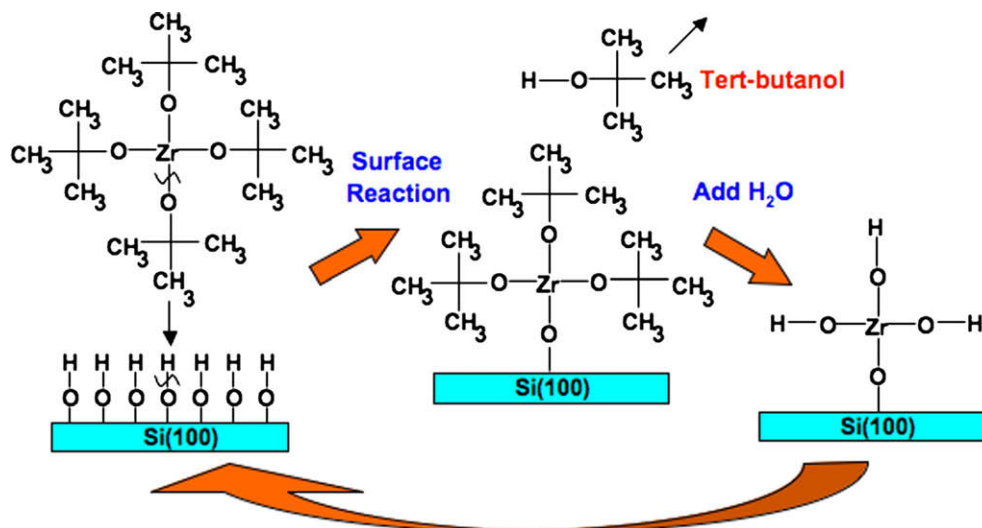


Fig. 1. Generally accepted ALD reaction mechanism for zirconium tetra-*tert*-butoxide and H₂O [4,9].

Finally, in order to fully evaluate the role of these released organic groups in the formation of surface carbon, it is necessary to determine the coverage and temperature dependence of the *tert*-butanol surface chemistry, since both of these dependencies would be expected to vary in a working ALD system.

In this letter we report on a UHV study of the surface chemistry of *tert*-butanol on Si(100)–(2 × 1) using coverage-dependent temperature-programmed desorption and Auger electron spectroscopy. Our Si samples have clean, fully reconstructed surfaces and thus, enabling us to examine to gather fundamental surface reaction data for bare silicon surfaces; in addition, the chemistry on this surface after exposure to atomic hydrogen from an *in situ* doser is also reported since the H-terminated surface is typical in a reaction environment. The study examines the chemisorption and desorption products of *tert*-butanol on this surface and relates the reaction mechanism to those expected from recent studies of the reactions of simple linear alcohols on this same surface.

2. Experimental methods

The experiments were performed in an UHV chamber equipped with a differentially pumped quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), a hemispherical-energy-analyzer-based Auger electron spectroscopy (AES) system, and an ion gun for sputter preparation and cleaning of the sample. The chamber had a typical base pressure of 10^{−9} Torr.

The Si(100) samples, with dimensions of 10 mm × 10 mm × 300 μm, were cut from p-type, B-doped, 0.001–0.01 Ω cm resistivity silicon wafers (Virginia semiconductor). The sample was fixed onto a molybdenum sample holder by molybdenum clips. The sample holder was then secured on a Boralectric heater, which was mounted on a stainless steel, liquid-nitrogen-cooled manipulator. The liquid-nitrogen-cooled manipulator allowed for cooling to temperatures down to 150 K. The Boralectric heater and manipulator were connected using molybdenum screws. The sample was uniformly heated to temperatures above 900 K by passing current through the heater. The temperature of the sample was measured by a K-type (chromel–alumel) thermocouple connected to the clips on the sample holder. The Si(100) sample was cleaned in the UHV system by repeated cycles of 2-keV Ar⁺ sputtering at room temperature and subsequent annealing at 1200 K for 5 min. The cleanliness of the sample was verified with AES and found to be free of contaminants. In addition, the appearance of hydrogen desorption

from an atomic-hydrogen-dosed surface (see below) served as an additional calibration of the silicon surface quality.

Our adsorbate, *tert*-butanol, is a neat liquid at room temperature; thus it was necessary to heat the pipeline to 323 K to ensure that the compound did not condense during delivery. The *tert*-butanol was purified by repeated freeze–pump–thaw cycles. The Si(100) samples were exposed to *tert*-butanol at 200 K by dosing directly onto the sample using a 2.5 μm-pinhole doser. The pinhole doser was placed inside 1/4" tubing, 5 mm away from the tip. The distance between the tip of the tube and the sample during exposure was ~1 mm. The pressure built up between the sample and the doser was estimated based on the geometry and the measured flow rate from the doser. The exposures given in this paper are calculated based on this estimated pressure build up in the region between the sample and the doser.

The QMS was fitted with a 3.35 mm-diameter aperture located directly in front of its ionizer. The sample was placed ~1 mm from this aperture during TPD measurements to ensure that only species desorbing directly from the sample were detected. A linear temperature ramp of 2 K/s was used for all TPD measurements. Prior to each *tert*-butanol exposure, the sample was sputtered with Ar⁺ and heated to 1200 K and then allowed to cool immediately. TPD data were collected with a computer program capable of monitoring 6 mass-to-charge ratios simultaneously.

The electron-beam energy used to obtain AES was 3 keV with a current density of ~0.04 μA/mm² at the surface. The Si(LMM) peak was routinely measured for each run and served as an energy and intensity reference for our Auger spectra. The AES signals generally remained unchanged, even after several AES measurement cycles, indicating that electron-induced desorption of the carbon and oxygen was negligible. Note that a relative sensitivity ratio of 2.5 for O to C was used based on Auger measurements on *tert*-butanol covered surfaces.

3. Results and discussion

3.1. Chemisorption of *tert*-butanol on clean Si(100)

Following full surface preparation and subsequent dosing of the surface with *tert*-butanol at 200 K, as described in the previous section, desorption spectra were obtained for several different exposures. After each exposure, a TPD spectrum was recorded, and the clean (2 × 1) surface was restored before the sample was re-

dosed with a, typically, increased exposure from the previous measurement. For each TPD ramp, several masses, including $m/e = 59$, 56, 43, 41, 39, 26, 15, and 2, were monitored by QMS; experimental data were then obtained for various values of surface exposure. The strongest spectral features were seen at $m/e = 41$ and 2. The data for these two m/e values are displayed for four values of exposure in Fig. 2. The dominant desorption peak for $m/e = 41$ was at ~ 640 K; this feature was observed on all samples with surfaces that were properly prepared and cleaned. In addition to the strong signal at $m/e = 41$, other secondary masses were also observed at 640 K, i.e. $m/e = 56$, 39 and 26. The relative ratio of these mass peaks, agrees well with that expected from electron-impact cracking of isobutene; the principal desorption product can thus be assigned to isobutene. The behavior of the $m/e = 41$ peak was studied as a function of exposure and was found to increase nearly linearly and then saturate at ~ 8 L and above; see inset in Fig. 2a. These peak temperatures and desorption curve shapes are generally in agreement with the results of Kim et al. [15]. In addition to the masses shown in Fig. 2, a very weak desorption feature at the main fragment of the parent molecule, i.e. $m/e = 59$, was observed at 380 K for high values of exposure, e.g. 90 L. Note that at this same temperature, peaks at $m/e = 41$ and $m/e = 2$ were also detected; these later two peaks are consistent with the expected fragmentation of the parent molecule. Thus the assignment of this peak to

some form of weak molecular desorbed feature as in Kim et al. is consistent with our results as well [15]. Finally, Fig. 2a also shows a small feature at $m/e = 41$ at 500 K. By monitoring TPD curves at several different sample positions, it was determined that this peak is from the sample mounting system.

The second major desorption feature, i.e. $m/e = 2$, which occurs at 790 K in Fig. 2b, is due to desorption of molecular hydrogen. Comparison with prior studies of atomic-hydrogen-exposed Si(100), to be described below, shows that the peak area is close to that known to be observed from a monolayer, hydrogen-covered Si(100) surfaces [16]. Note, however, that the peak temperature is slightly higher than that measured in these prior reports of purely hydrogen-exposed surfaces and discussed below for our own comparative experiments of H_2 desorption from clean Si(100); this small change is attributed to the fact that the desorption does not proceed from a hydrogen-terminated surface but rather from a mixed phase of a hydrogen- and OH-terminated surface. A previous study of D_2 desorption from a D_2O -exposed Si(100) surface found a similar shift in the peak position [17]. In addition, a small feature at 647 K was also observed at high, i.e. >17 L, *tert*-butanol exposures. This temperature is consistent with formation of the Si dihydride species after completion of monohydride-site filling [16], which would occur at large surface concentrations of *tert*-butoxy.

3.2. Surface carbon after desorption of *tert*-butanol

Auger spectroscopic (AES) measurements were made in order to determine the presence of any surface-bound species remaining after thermal ramping. Specifically, after the Si surface was exposed to *tert*-butanol and then ramped to 725 K, AES of the surface was taken; in comparison to the AES of the clean surface, the presence of added C and O was measured. A relative measurement of this carbon concentration, using the carbon KLL Auger signal, is shown in Fig. 3 for a series of surface exposures, from 0.08 L to 19.4 L of *tert*-butanol, followed by thermal ramping. The data show that the surface coverage of carbon increases at first rapidly with coverage and then saturates at ~ 8 L. Note that the saturation exposure is approximately the same as that of *tert*-butanol, shown in inset of Fig. 2a. These results show clearly that exposure of the Si surface to *tert*-butanol results in significant surface carbon coverage despite substantial loss of adsorbed hydrocarbons, principally through desorbing isobutene after thermal ramping. In addition, measurement of the oxygen KLL spectra as a function of the coverage (not shown) indicates that chemisorbed oxygen also increased as a result of *tert*-butanol exposure and desorption. In addition, the C/O ratio, determined using careful Auger measurements, was found to be a constant value of 0.68 ± 0.07 as shown for the three averaged points in the inset of Fig. 3b.

3.3. Effect of surface termination on the *tert*-butanol surface chemistry

Several previous studies of ALD on Si have used hydrogen passivation of the silicon surface to minimize oxidation on the silicon prior to ALD growth [5,7,18,19]. For example, by employing various surface technique tools, Gusev et al. were able to obtain an abrupt interface between a hydrofluoric-acid(HF)-treated silicon surface and a ~ 2.4 nm Al_2O_3 ALD-grown layer [7]. In addition, others have examined directly whether surface hydrogenation can enhance ALD growth. For example, one investigation of ALD growth of Al_2O_3 showed that initial deposition begins with the reaction between the metal-organic precursor and the hydrogen-treated-sample surface [2]. However, the work by Kelly et al. [18] actually suggests that there is essentially no reactivity observed on H-terminated silicon with respect to the dimethyl(amido)-functionalized precursors and the surface reactivity is governed by defects.

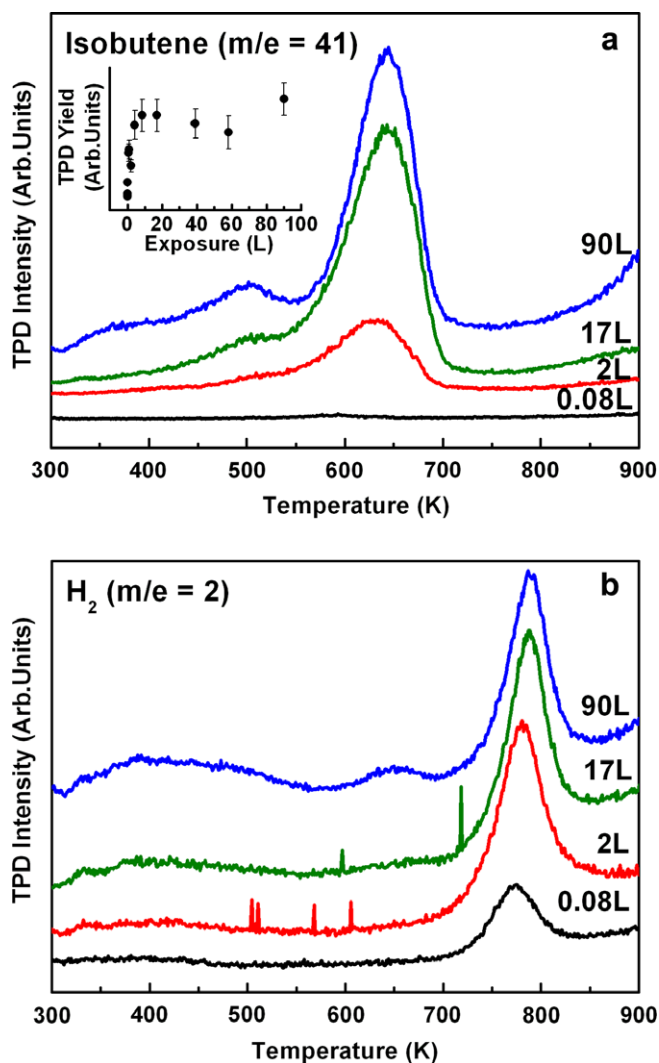


Fig. 2. Temperature programmed desorption spectra of *tert*-butanol (a) for $m/e = 41$ and (b) for $m/e = 2$ on Si(100) surface for four values of initial exposure.

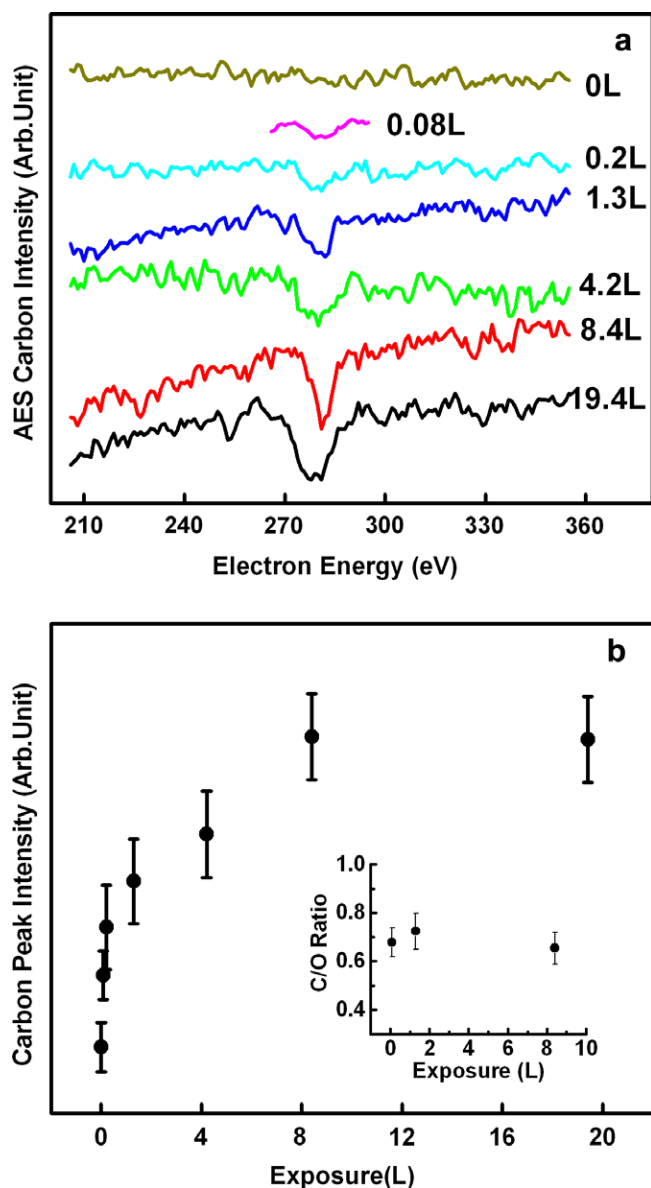


Fig. 3. (a) Auger electron signal for C(KLL) from a Si surface after exposure of the surface to *tert*-butanol, followed then by thermal ramping to 725 K. (b) The peak carbon signal as a function of exposure to *tert*-butanol. The inset shows the measured C/O ratio based on careful Auger measurements of C and O versus exposure of *tert*-butanol.

These experiments yielded a detailed understanding of the resulting surface reactions of several possible precursors with the Si surfaces and shown that this interfacial region plays a major role in the electrical and materials properties of the final dielectric layer. Note that these experiments were focused on examining reactions on *ex situ* prepared hydrogenated surface and thus reactions on the bare surface were not examined using UHV tools. In our experiments below, we form a hydrogen-terminated Si(100) surface *in situ* and examine how its formation influences the surface chemistry from of any *tert*-butanol, which might be present during the initial cycle of ALD. Examining surface reactions in the presence of H-terminated surface is important for understanding the state and conditions for forming a useful interfacial layer, as well as for understanding how H-termination might effect *tert*-butanol reactions during ALD.

With these motivating factors in mind, a monolayer of hydrogen on Si(100) was prepared *in-situ* by exposing the surface to

atomic hydrogen, formed from a tungsten filament, at a sample temperature of 650 K [20,21], to create a similar surface to that of a hydrofluoric-acid-functionalized surface, which is sometimes used in the first monolayer of growth using ZTB [5]. This temperature prevents the formation of the Si dihydride species since this species desorbs at surface temperatures higher than $T = 600$ K [21]. TPD from such a sample after 17 L of *tert*-butanol exposure is shown in Fig. 4a. Compared to signal obtained for the same exposure of a clean Si surface, a dramatically reduced isobutene desorption signal is observed due to hydrogen passivation of the surface. Note the desorption peak from the sample mounting system now appears at 435 K instead of 500 K in Fig. 2a; we attribute this shift to a small change in the thermal contact resistance of the holder with the heat sink. The corresponding hydrogen TPD curves are given in Fig. 4b along with a TPD spectrum from a 1-ML hydrogen-terminated surface for reference. TPD signals for both of these hydrogen-terminated surfaces are identical within experimental error. By comparison, the peak signal from the *tert*-butanol-exposed bare silicon sample indicated a coverage of 88% of that from the purely hydrogen-passivated surface. A similar difference had

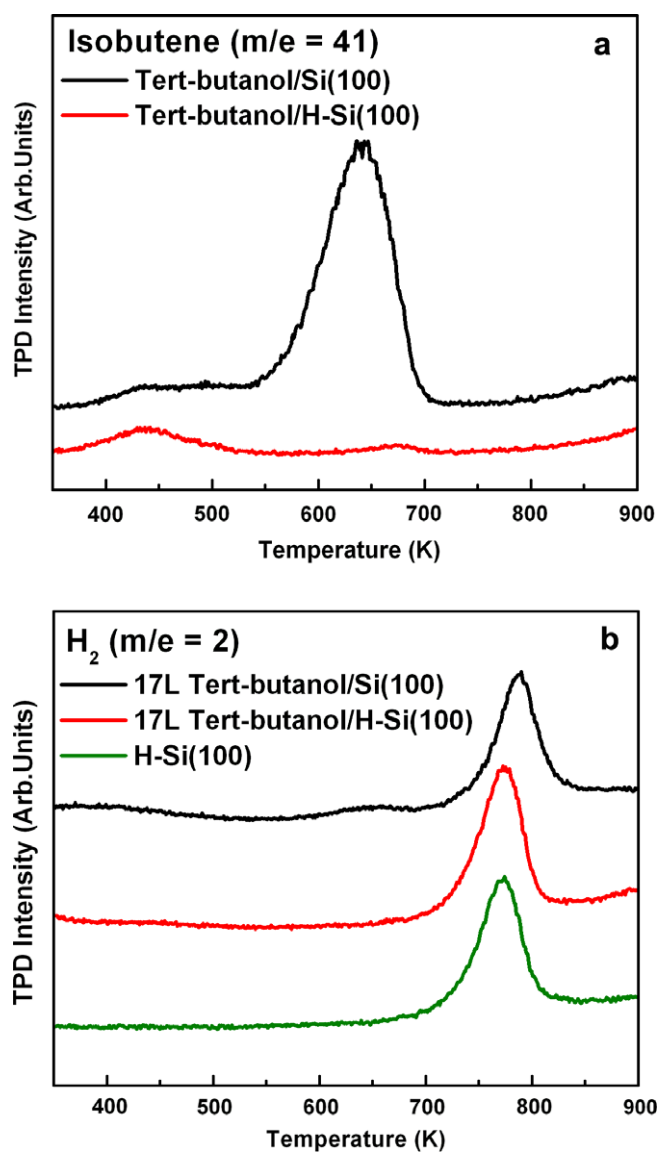


Fig. 4. TPD spectra of (a) $m/e = 41$ and (b) $m/e = 2$ from H-Si(100) and bare Si(100) surface after 17 L of *tert*-butanol exposure. In addition, panel (b) contains a TPD spectrum at $m/e = 2$ from a Si surface exposed to atomic hydrogen for comparison.

previously been observed for the case of D_2O chemisorbing on Si; in this case the peak signals from a H-dosed clean Si surface were compared to those from dissociatively adsorbed D_2O -covered Si- (2×1) [17]. In the case of D_2O , this difference, which suggested less than full-monolayer of H-atom coverage, was attributed to unoccupied sites resulting from D and OD adsorbed across diagonally adjacent dangling bonds. Such site filling would be expected to be present in our case of *tert*-butanol adsorption, in which H and *tert*-butoxy group adsorb on two separate dimers. In addition, as discussed later in Section 3.5, site blocking due to surface carbon deposit ion reduces the hydrogen yield.

3.4. Surface-reaction mechanism

The large body of previous work on the reactions of other alcohols on Si(100)- (2×1) surfaces can be used to aid the interpretation of our product observations [22–26]. Consider first dissociative adsorption of methanol (CH_3OH) on Si(100) at 300 K. For this process, high-resolution core-level photoemission has shown that dissociative chemisorption of CH_3OH proceeds via O–H bond cleavage to form terminal methoxy and H species [23] and, in fact, the resulting surface methoxy species were also seen directly using infrared reflection spectroscopy [26]. In the case of ethanol (C_2H_5OH), Casaletto et al. [22] also showed using core-level photoemission spectroscopy that this same bond-cleavage process dominated the chemisorption step to yield terminal Si–H and Si– OC_2H_5 species. Further infrared spectroscopy suggested that these products are bound to opposite atoms of a single dimer rather than to two different dimers of the Si(100)- (2×1) surface [25]. In this arrangement the ethoxy is bound to the lower, partial positively charged Si atom.

In addition, results using TPD mass spectroscopy confirm these observations but also suggest that the surface chemistry becomes more complex in heavier alcohols; of course, such TPD measurements also determine the thermal desorption products. For example, TPD measurements have probed the chemisorption products of methanol, ethanol, and 1-propanol on Si(100) [24]; these same TPD studies were amplified by accompanying DFT cluster calculations on the reaction mechanism [18]. For each of these alcohols, desorption of the terminal alkoxy group was found to occur via β -H elimination, at 630 K, to release the corresponding aldehyde. In addition, desorbed hydrogen, SiO, and CH_x were reported at 825 K, 950 K, and 790 K, respectively. The latter two products suggest the presence (and decomposition) of a surface-bound species due to a minority reaction channel. Thus for simple alcohols, β -H elimination of alkoxy radicals, to form aldehyde groups, appears to be the main channel of desorption. However, for more complex alcohols other simultaneous or parallel desorption pathways have also been shown to exist. For example, in the case of 1-propanol, the observation of propylene in the desorption spectra was attributed to C–H bond cleavage, via β -H elimination, followed by removal of OH during desorption of the adsorbed species to yield the alkene product [24]. We note in passing that this same mechanism has recently been shown to lead to C–H facile bond cleavage for organometallic precursors and is well known, as well for tertiary amines [27–29].

The basic reaction mechanism of *tert*-butanol can be interpreted in light of these prior results with simple alcohols and using our experimental observations. First, as was the case with simple alcohols, our parent molecule was not present among the desorption products in the low exposure regime; this is a result of the nonreversible dissociative adsorption of *tert*-butanol on the Si(100)- 2×1 surface. Second, molecular-hydrogen desorption was observed at ~ 790 K for our experiments just as has been reported in TPD measurements using simple alcohols. However, unlike these prior experiments, formation of an aldehyde through

simple loss of hydrogen is not possible for *tert*-butanol. In agreement with this expectation, we only observed isobutene desorption. Third, as expected from the absence of O-containing species in the TPD products, we do observe significant surface O in the Auger measurements.

Our observations are sketched in Fig. 5 using a surface-reaction scheme, which is similar to that of Kim et al. [15]; our results may be summarized as follows: First, *tert*-butanol chemisorption dominantly proceed via an addition reaction involving O–H bond cleavage to yield terminal surface hydrogen and *tert*-butoxy. Based on the prior calculations and observations of this addition reaction involving the three linear alcohols [24,25], mentioned above, these species are likely to be bound on the opposite dangling bonds of the same dimer. Note that this configuration is energetically more favorable than these two products occupying two separate dimers and is in accord with the partial charging on each dimer atom. Also in line with the short comment earlier in this section, it is not possible to rule out a contribution to isobutene formation from adsorption of *tert*-butanol via C–H dissociation followed by C–O bond cleavage during desorption. Second, the formation of isobutene requires breaking the O–C bond and one H–C bond. By analogy with recently studied reactions of, say, 1-propanol with Si dimers to form propylene, the reaction could be initiated by β -H elimination. This process is known to lead to a characteristic desorption temperature of 630 K for a wide variety of organic-molecule reactions on Si dimers. The reaction could proceed either in a single, concerted step, during which a hydrogen atom is captured by the oxygen to yield a desorbed isobutene molecule or through formation of an intermediate surface-bound species. TPD experiments alone cannot determine whether such a surface-bound isobutene species exists or not. In any case, O–C and H–C bond cleavage results in desorption of isobutene at ~ 640 K. Finally, from prior experiments with H_2O on Si(100)- (2×1) [30] and D_2O on Si(100)- (2×1) [31], it is known that the OH bound to Si at room temperature dissociates at ~ 500 K to form Si–O–Si and Si–H bonds; thus in our experiments, any oxygen and hydrogen atoms left on the surface upon isobutene desorption would be expected also to be bound in these configurations. The similarity of the hydrogen desorption peaks in our experiments and those from experiments on water-decorated Si(100) surfaces suggests that,

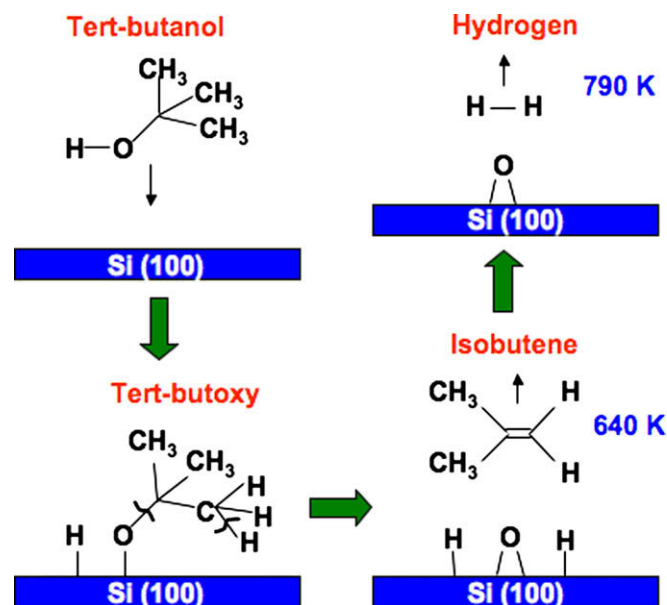


Fig. 5. Summary of proposed, dominant surface decomposition reactions for *tert*-butanol on a clean Si(100) surface.

in fact, our surface configurations after isobutene desorption are very similar to those obtained with water-dosed Si.

3.5. Carbon formation on Si(100)

Our AES data have shown a rapid surface carbon-signal increase at low exposures and thermal desorption to 725 K; this increase is also seen in the surface-oxygen Auger signal. Our TPD results give additional insight into the origin of this low-coverage surface carbonization. Recall that in Fig. 2 evidence of saturation of the desorption signal was seen at high exposure. In particular, for exposures >8 L, the isobutene desorption peak saturated; however the first-monolayer hydrogen yield saturated at much lower exposure. This difference in the saturation coverage of the two desorbing species can be explained by taking complete decomposition of a partial fraction of the adsorbed *tert*-butanol molecules into account. Such a decomposition would result in one oxygen, four carbon, and nine hydrogen atoms to the surface and the first monolayer hydrogen peak at ~790 K would be expected to saturate earlier than isobutene peak. On the other hand, the Auger data of carbon shown in Fig. 3b saturates at about the same exposure as for isobutene and the C/O ratio does not change within the studied exposure region indicating constant decomposition probability for the studied exposure range. The measured C/O ratio suggests that ~17% of the *tert*-butanol adsorbed on the first monolayer has undergone surface decomposition rather than desorbing as isobutene. Furthermore, site blocking by as-deposited carbon can be an additional contributing factor to the decrease in the hydrogen desorption feature, discussed in Section 3.3. The amount of reduction is modest (12%), compared to the amount of carbon deposited on the surface. However, the exact details of the adsorbed moiety are not known at this time. Thus, carbon or carbon species may adsorb via a bridging site of the Si dimer leaving two dangling bonds available for hydrogen to bond. Finally, evidence for decomposition of simple alcohols on clean Si(100) has been previously discussed [22–26]. The origin of this decomposition was thought to involve C–O bond cleavage of the surface-bound alkoxy group. It is reasonable that a similar reaction pathway would exist for *tert*-butoxy.

4. Conclusion

In this paper UHV probes have been used to investigate the reaction of an important decomposition product, i.e. *tert*-butanol, of the ALD precursor, ZTB with a Si(100) surface. Our TPD studies have shown isobutene and hydrogen are the main desorption species from *tert*-butanol exposed clean Si(100)–(2 × 1). On the other hand, a single monolayer hydrogen-terminated surface shows no reactivity to *tert*-butanol. Finally, our AES results show clear evidence of carbon deposition during *tert*-butanol exposure on clean silicon; this appears to originate from the dehydrogenation of the

surface-bound *tert*-butoxy groups before desorption can occur. Note that in ALD deposition, this undesired surface reaction by released ligands will be reduced or enhanced depending on the presence of any surface site blockers on the Si surface.

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