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JVST A

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Vacuum, Surfaces, and Films

Papers from the
40th National Symposium of the
American Vacuum Society, Part I

Part I
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Electronic Materials
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Kinetic and mechanistic study of the chemical vapor deposition of titanium dioxide thin films using tetrakis-(isopropoxo)-titanium(IV)

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Center for Interfacial Engineering and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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The mechanism of TiO_2 thin film deposition on single crystal TiO_2 by chemical vapor deposition (CVD) using tetrakis(isopropoxo)titanium(IV) (TTIP) has been investigated. The structure of the rutile(100) surface has been shown to form a 1×3 reconstruction using reflection high-energy electron diffraction. Temperature programmed reaction spectroscopy and molecular beam scattering have been employed to probe the kinetics of the reaction of TTIP and to identify reaction products. The deposition mechanism involves two parallel pathways to form TiO_2: at lower temperatures (500–650 K) propene and isopropanol are formed as products; at higher temperatures (>650 K) propene and water are formed as products in a second pathway that becomes dominant. An activation energy of 57 ± 8 kJ/mol has been measured for the first pathway. The results for the single crystal surface are compared to earlier work on polycrystalline substrates.

I. INTRODUCTION

Titanium dioxide (TiO_2) has been proposed as a material for use as a dielectric insulator in metal oxide semiconductors (MOS) for a variety of applications including memory devices, dielectric filter stacks,[1,2] and chemically resistant antireflective coatings for optical devices[3,4] because of its high dielectric constant, its chemical stability, and its optical transparency in the visible and near infrared regions.

Particularly in the fabrication of microelectronic devices, the chemical vapor deposition (CVD) of TiO_2 is of interest to accommodate the decreasing size of features and ease of control over deposition conditions.[2,5] However, the physical and chemical properties of the CVD precursors are infrequently related to the resultant properties of the deposited films such that full control over the deposition can be established.

The CVD of TiO_2 has been studied using a variety of precursors, focusing primarily on titanium tetrachloride ($TiCl_4$) plus water[4] or titanium alkoxides [$Ti(OR)_4$, where R=ethyl or isopropyl].[1–3,5,6] Most widely reported are studies of the structure and properties of the deposited films, rather than the mechanistic chemistry of the deposition reactions.

In this paper, the relationship between the structure of the deposited TiO_2 film and the chemistry of the deposition process using tetrakis-(isopropoxo)-titanium(IV) (TTIP) as a precursor has been investigated. We have focused on epitaxial growth because of the influence of this chemistry on the formation of defects in the films which must be finely controlled in the fabrication of devices used in technological applications.[7,8]

II. EXPERIMENT

The temperature programmed desorption (TPD), molecular beam scattering (MBS), and reflection high-energy electron diffraction (RHEED) experiments were performed in the two chamber ultrahigh vacuum (UHV) CVD/thin film characterization system illustrated in Fig. 1. The main chamber (~60 L) was pumped by a 510 L/s (N_2) Balzers turbomolecular pump and a titanium sublimation pump. The chamber was arranged in three levels. The lowest level was equipped with a Physical Electronics Model 15-255G double pass cylindrical mirror analyzer (CMA) which was used for Auger electron spectroscopy (AES). The intermediate level was used for sample transfer between the two chambers. The upper level was equipped with a differentially pumped Extrel C50 quadrupole mass spectrometer (QMS) with a mass range of 2–750 amu, which was used for the TPD and MBS experiments. The QMS was separated from the main chamber by a skimmer with a 3 mm orifice in front of which the sample was placed for the TPD experiments. The QMS chamber (~7 L) was pumped by a 170 L/s (N_2) Balzers turbomolecular pump. The upper level also includes a Physical Electronics 04-303A 5 kV ion gun which was differentially pumped through the QMS chamber. Argon was used for all the sputtering. The main chamber had a base pressure of 2×10^{-10} Torr and an operating pressure of about 2×10^{-9} Torr. The QMS chamber had a base pressure of $\sim1\times10^{-9}$ Torr.

The reactor chamber (~20 L) was pumped by a 170 L/s Balzers turbomolecular pump and a titanium sublimation pump. It was equipped with a Physical Electronics 06-190 electron gun (10 kV) used for RHEED experiments. The diffraction patterns were displayed on a phosphor screen located 20 ± 1 cm from the sample. The electron beam was focused onto the sample at an angle of 1.5°–2° from the surface plane. Patterns were recorded using a Polaroid camera. Lattice constants were determined using GaAs(100) as a reference. The base pressure of this chamber was typically 1×10^{-9} Torr and could be operated as high as 1×10^{-5} Torr for CVD experiments.

The reactor and main chambers were connected via a 4 in. gate valve. The reactor was attached via a $2\frac{3}{4}$ in. gate valve to a six-way cross used for a load lock to allow for quick transfer of samples in and out of the UHV system. Transfer of samples into the reactor, and between the chambers, were made using magnetically coupled transfer rods. The sample

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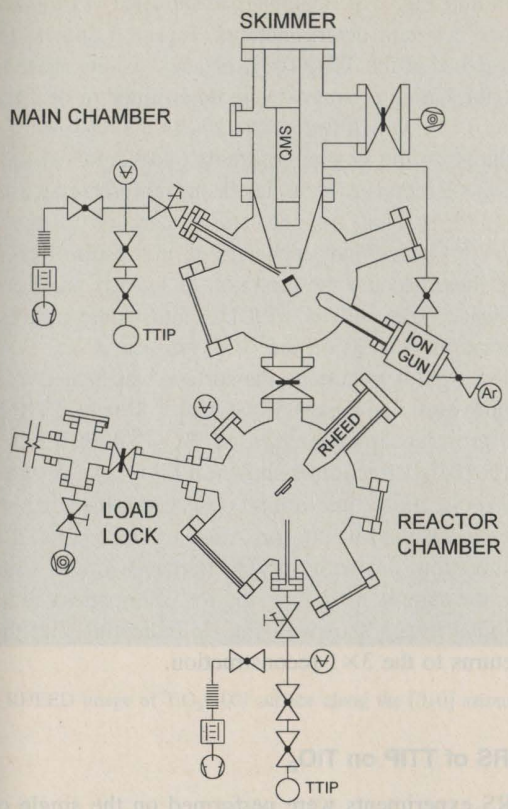

FIG. 1. Diagram of the CVD-TF system.

manipulators used in the system were capable of x, y, and z linear motions with z axis and azimuthal rotations.

Two types of sample mounts were used in the system. RHEED experiments were done by mounting the sample onto a molybdenum disk which was designed for use with the transfer system. The sample was held in place with a molybdenum clip using indium between the sample and disk as a thermal contact. These samples were heated from the back side of the disk via an electron beam heater. The sample temperature was monitored using an optical pyrometer which viewed the sample from outside the system. Temperatures in the range of 273–1073 K were attainable using this arrangement. However, increasing the temperature above 873 K resulted in the evaporation of indium from beneath the sample, with the resultant loss of thermal contact.

A second sample mount was used for the temperature programmed reaction spectroscopy (TPRS) and MBS experiments. It consisted of a U-shaped tantalum foil (0.23 mm thick) attached to a copper block which was in thermal contact with a liquid nitrogen reservoir. The sample was clamped to the tantalum foil with molybdenum clips and the temperature of the sample was measured using a chromel-alumel (K-type) thermocouple clamped between the molybdenum clip and the surface of the sample. The sample was radiatively heated from the back side using a tungsten filament powered by a manually controlled 120 V ac variable transformer. In this configuration temperatures in the range from 195 to 1073 K and heating rates of up to 20 K/s were possible. This mount was used only in the main chamber, and did not allow for sample transfer between the two chambers. For TPD experiments, the sample was placed ~5 mm from the end of the doser (described below) for adsorption of the precursor onto the substrate. It was then moved to a position ~1 mm in front of the orifice of the skimmer for the temperature ramp. In the MBS experiments, the sample was located at the point where the center axes of the doser and QMS housing intersect; meanwhile, a constant flux of precursor was impinged on the substrate throughout the temperature ramp.

TiO_2 (rutile) single crystals (12 mm×12 mm×1 mm) in the (100) orientation (Commercial Crystal Laboratories) were used for the TPD, MBS, and RHEED experiments. It was found that reproducible TPD and MBS experiments on a given crystal could be achieved only after the procedure reported by Muryn *et al.*[9] was performed. This involved sputtering the surface using 5 kV Ar^+ for 20–30 min and then annealing at ~1100 K for 20 min in vacuum. This treatment changed the color of the crystal from a pale transparent yellow to an opaque metallic gray, consistent with the observations reported by Muryn *et al.*, in which they concluded that the presence of surface defects in the form of the 3×1 reconstruction has negligible effects on the reactivity of H_2O. The gray color is also consistent with the formation of crystallographic shear planes associated with the loss of small amounts of oxygen from the bulk.[10]

AES spectra were acquired using an electron energy of 3 kV in the counting mode [$N(E)$]. These spectra were then differentiated mathematically using the Savitsky–Golay differentiation algorithm. Mass spectra were taken using an electron energy of 30 eV to minimize fragmentation of the precursor. Both the CMA and the QMS were controlled by a Zenith 386 microcomputer. The CMA was interfaced via a Physical Electronics Model 137 adapter card and software which controls the CMA and provides some data manipulation capabilities. The QMS was interfaced using a Metrabyte DAS-HRES data acquisition board which controls the mass selection on the QMS and reads the analog output of the QMS as well as the thermocouple output from the sample using software written in house.

The dosers and gas manifolds used on the system were constructed of $\frac{1}{4}$ in. stainless steel VCR components. The manifold was pumped by an Alcatel 2020A rotary vane pump (26.9 m^3/h) with a MDC molecular sieve trap. The precursor vessel was a glass bulb made from a glass to stainless steel transition attached to a stainless steel tube which connects to a Nupro valve which was used to isolate the tube. The pressure in the manifold was measured using a MKS Baratron capacitance manometer (Model 315B, 10 Torr range). The manifold was attached to the chamber via a Varian leak valve. The doser was a $\frac{1}{4}$ in. o.d. stainless steel tube. The precursor was outgassed by three freeze–pump–thaw cycles using ice water as the coolant. During TPD and MBS experiments the manifold (but not the precursor vessel) was heated to ~80 °C to prevent condensation of the precursor. The isolation valve was left open during dosing with the pressure in the manifold controlled by partially closing the valve between the manifold and the pump. The manifold

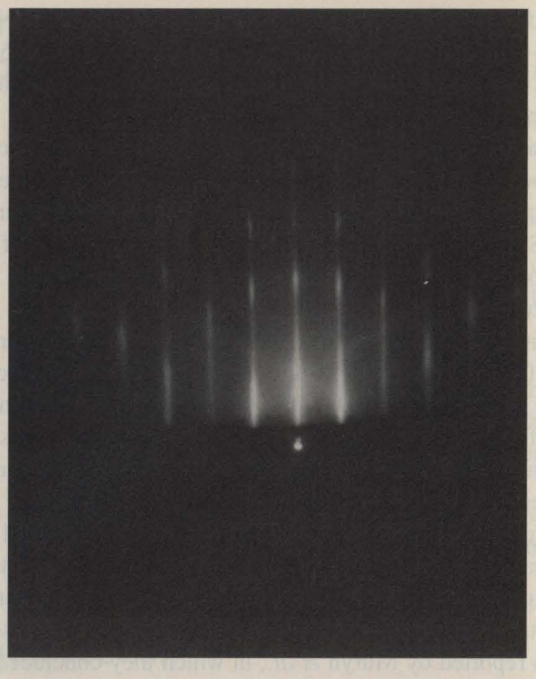

FIG. 2. RHEED image of the annealed $TiO_2(100)$ surface along the [010] azimuth.

pressure was maintained between 15 and 20 mTorr by this method.

III. RESULTS AND DISCUSSION

A. RHEED of $TiO_2(100)$

RHEED photographs of the (100) surface are shown in Figs. 2 and 3. Figure 2 is the pattern attributed to the [010] azimuth and Fig. 3 is attributed to the [001] azimuth based on lattice constant determinations. Figure 4 shows the surface structure of the $TiO_2(100)$ surface.[11] Using these photographs, the lattice constants were determined to be 14.5 ± 0.5 Å$\times3.0\pm0.1$ Å, which is consistent with a 3×1 surface structure relative to the known constants (4.49 Å$\times$2.96 Å).[11]

FIG. 3. RHEED image of the annealed $TiO_2(100)$ surface along the [001] azimuth.

This 3×1 reconstruction has been interpreted as a loss of every third row of oxygen atoms parallel to the [001] direction.[9,12] It does not appear to be the result of crystallographic shear because the direction of shear is parallel to the (100) surface (the shift is $1/2\langle011\rangle$) and would not result in the formation of steps on the (100) surface.

Following this treatment, the surface was heated to 873 K in vacuum and then exposed to 1×10^{-6} Torr of TTIP for 15 min to grow an epitaxial film of TiO_2.[7] A RHEED photo along the [010] direction is shown in Fig. 5. An image along the [001] direction could not be observed. This suggests that the growth resulted in the formation of steps parallel to the [001] direction, but with varying terrace widths.[9] Upon annealing the sample as before, the RHEED pattern returns to the original image shown in Fig. 2, indicating that the surface returns to the 3×1 reconstruction.

B. TPRS of TTIP on TiO_2

TPRS experiments were performed on the single crystal $TiO_2(100)$ surface using TTIP. In these experiments ~20 L was adsorbed onto the TiO_2 surface at about 343 K.[13] Then the temperature of the sample was increased to about 973 K at a constant rate of 5 K/s. The results of this experiment are shown in Fig. 6.

The following ion fragments were monitored during the TPRS and MBS experiments: TTIP, $m/e=225$; propene, $m/e=39$; isopropanol, $m/e=45$; water, $m/e=18$; and acetone, $m/e=43$. The ion fragments used were selected because of minimal ovarlap of daughter ion masses which originate from different molecular species. Isopropanol was corrected for a contribution from TTIP and acetone was corrected for contributions from both isopropanol and TTIP.

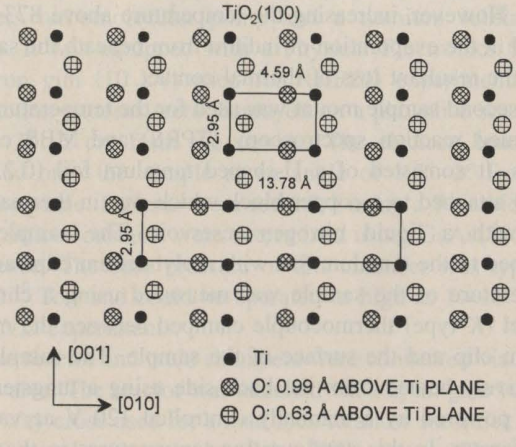

FIG. 4. Diagram of $TiO_2(100)$ surface showing [010] and [001] azimuthal directions.

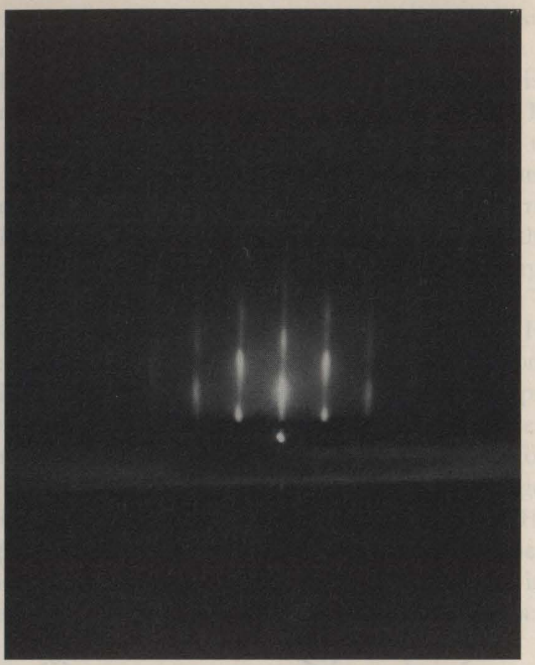

FIG. 5. RHEED image of TiO_2(100) surface along the [010] azimuth after CVD.

The data shows that no TTIP is desorbed under these conditions, indicating that the monolayer deposited at 343 K is adsorbed irreversibly. Propene and isopropanol are the only products observed in the TPRS experiment.

In control experiments using isopropanol as the adsorbate it was observed that isopropanol desorbs molecularly below 423 K. Propene would not adsorb onto the TiO_2 substrate at the lowest temperatures attempted here (193 K). Malet and Munuera[14] performed TPD experiments with water on rutile powders and found that water will dissociatively adsorb to form surface hydroxyl groups, which desorb as water with a peak temperature of 590 K. In the TPRS experiment with TTIP, the desorption of propene and isopropanol are not the rate limiting steps, suggesting that one of the reaction steps is rate limiting. Also, propene and isopropanol peaks track each other closely, indicating that the rate limiting step forms both species simultaneously.

Using the first order kinetic model of Redhead,[15] with an assumed preexponential value of 10^{12} and an experimental heating rate of 5.3 K/s, the activation energy is 134±2 kJ/mol. This value is similar to that of Wu *et al.*.[16] (130–135 kJ/mol) and suggests that the rate limiting chemistry is similar in both cases.

C. MBS of TTIP on TiO_2(100)

MBS experiments were performed using TTIP on the single crystal TiO_2(100) surface. The experiment is performed by increasing the temperature of the sample from ~70 to ~600 °C at a constant rate of 2 K/s and then allowing the sample to cool with the radiative heater off, while maintaining a constant flux of precursor and monitoring the precursor and reaction products using the QMS.

The data for a flux of 1×10^{-6} Torr TTIP is shown in Fig. 7, showing signal for the precursor TTIP and the primary

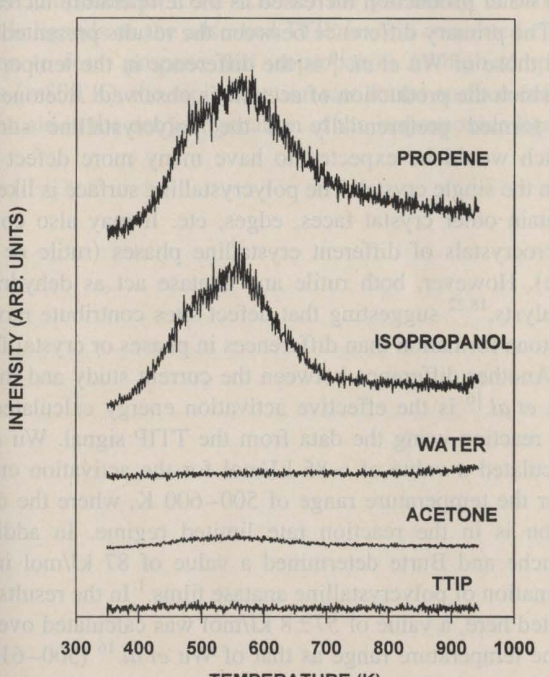

FIG. 6. TPRS spectrum of TTIP after a dose of 20 L and using a 5.3 K/s heating rate.

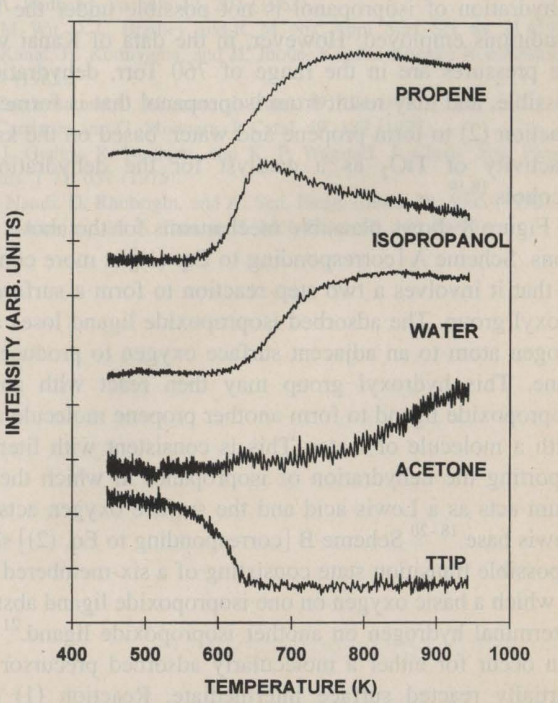

FIG. 7. MBS data for TTIP. The following fragments were monitored to give the resultant data: TTIP, m/e=225; propene, m/e=39; isopropanol, m/e=45 (corrected for contribution from TTIP); water, m/e=18; and acetone, m/e=43 (corrected for contributions from isopropanol and TTIP). These were chosen for the minimal mutual overlap. The data are shown for a TTIP pressure of 1×10^{-6} Torr.

products propene, isopropanol, water, and acetone. The rate of the reaction becomes significant above 530 K and all of the precursor is consumed by 640 K. The most striking feature is observed in the product profile for isopropanol. Here the signal intensity increases above 570 K, similar to propene, but reaches a maximum near 660 K, and then decreases at higher temperatures. In the profile for water, the signal intensity does not start to increase until the temperature rises above 610 K. Because these temperatures do not coincide, and because the TPRS data shows that water is not formed when isopropanol is generated, we conclude that there are different, parallel reaction pathways which generate isopropanol and propene separately from water and propene.

Kanai *et al.*[17] reported a reaction stoichiometry for the formation of particles of TiO_2 in the gas phase using TTIP. They determined that the only products in addition to TiO_2 were propene and water from which they identified the following reaction:

$$Ti(OC_3H_7)_4 \rightarrow TiO_2 + 4C_3H_6 + 2H_2O. \quad (1)$$

This stoichiometry is consistent with our results in the higher temperature regime where little isopropanol is formed. It does not account for the production of isopropanol. The corresponding stoichiometry for the reaction of TTIP to form propene and isopropanol is

$$Ti(OC_3H_7)_4 \rightarrow TiO_2 + 2C_3H_6 + 2HOC_3H_7. \quad (2)$$

The conclusion of parallel reaction pathways requires the consideration of both of these reactions to form the observed products. These reactions must act independently because the dehydration of isopropanol is not possible under the UHV conditions employed. However, in the data of Kanai where the pressures are in the range of 760 Torr, dehydration is possible, and may result from isopropanol that is formed via reaction (2) to form propene and water, based on the known reactivity of TiO_2 as a catalyst for the dehydration of alcohols.[18,19]

Figure 8 shows plausible mechanisms for the above reactions. Scheme A [corresponding to Eq. (1)] is more complex in that it involves a two step reaction to form a surface hydroxyl group. The adsorbed isopropoxide ligand loses a hydrogen atom to an adjacent surface oxygen to produce propene. This hydroxyl group may then react with another isopropoxide ligand to form another propene molecule along with a molecule of water. This is consistent with literature reporting the dehydration of isopropanol in which the titanium acts as a Lewis acid and the surface oxygen acts as a Lewis base.[18–20] Scheme B [corresponding to Eq. (2)] shows a possible transition state consisting of a six-membered ring, in which a basic oxygen on one isopropoxide ligand abstracts a terminal hydrogen on another isopropoxide ligand.[21] This can occur for either a molecularly adsorbed precursor or a partially reacted surface intermediate. Reaction (1) commences at a higher temperature than reaction (2) because the abstraction of hydrogen to the surface is less facile than the formation of the six-membered intermediate.

Wu *et al.*[16] have done MBS experiments similar to those described above. They used a polycrystalline TiO_2 substrate prepared by CVD and observed the formation of acetone,

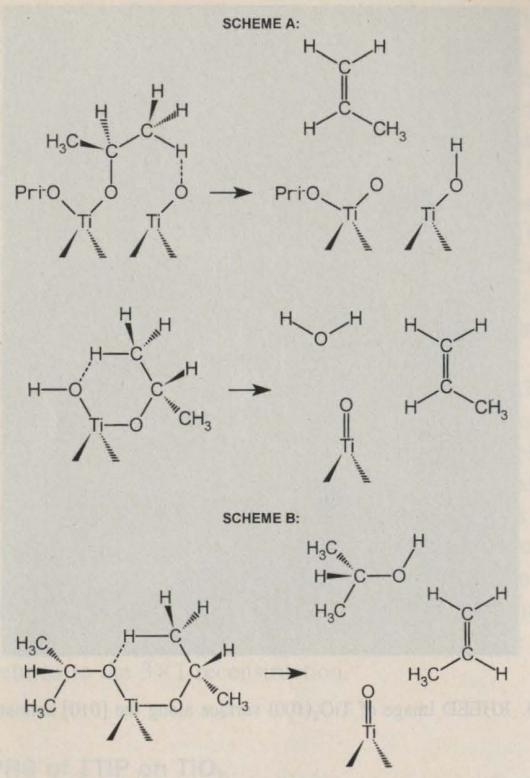

FIG. 8. Mechanistic schemes for reactions (1) and (2) in the CVD of TiO_2 using TTIP.

isopropanol, propene, and water over the temperature range of 500–800 K. They also noted the decrease of isopropanol and acetone signals above 650 K, while the rates of propene and water production increased as the temperature increased.

The primary difference between the results presented here and those of Wu *et al.*[16] is the difference in the temperature at which the production of acetone is observed. Acetone may be formed preferentially on the polycrystalline surface, which would be expected to have many more defect sites than the single crystal. The polycrystalline surface is likely to contain other crystal faces, edges, etc. It may also contain microcrystals of different crystalline phases (rutile or anatase). However, both rutile and anatase act as dehydration catalysts,[18,22] suggesting that defect sites contribute more to acetone formation than differences in phases or crystal faces.

Another difference between the current study and that of Wu *et al.*[16] is the effective activation energy calculated for the reaction using the data from the TTIP signal. Wu *et al.* calculated a value of ~85 kJ/mol for the activation energy over the temperature range of 500–600 K, where the deposition is in the reaction rate limited regime. In addition, Rauche and Burte determined a value of 87 kJ/mol in the formation of polycrystalline anatase films.[1] In the results presented here, a value of 57 ± 8 kJ/mol was calculated over the same temperature range as that of Wu *et al.*[16] (500–610 K) by the method they described using a first order fit. This difference in activation energies is be due to the differences in surface structure, either from the defects of the polycrystalline surface or from the difference in surface structure be-

tween rutile and anatase. An analysis of the data using a second order equation gives a poorer fit to the data.

This value for the activation energy (57±8 kJ/mol) is significantly different than the value determined from the TPRS data (134±2 kJ/mol). If the TPRS data are analyzed using E_a=57±8 kJ/mol, the preexponential factor is found to range from 4×10^3 to 2×10^5 s^{-1}. For comparison, Carrizosa and Munuera[18] have performed TPRS experiments with isopropanol on anatase and measured an activation energy of 92±2 kJ/mol and a preexponential factor of 4.7×10^6 s^{-1} for the formation of propene. The two schemes shown in Fig. 8 are consistent with a low activation barrier deriving from the relatively stable six-membered ring and with the low preexponential factor associated with the proposed rearrangement of the same (a result of multiple bond rupture and formation). The reactant molecule infrequently accesses this geometry via the random motion of the ligands on the TTIP. Hence the preexponential factor, which is a measure of the frequency at which the low energy activated complex is accessed, is small relative to the typical frequencies associated with molecular vibrations ($\sim10^{13}$ s^{-1}).

IV. CONCLUSIONS

The CVD of TiO_2 using TTIP has been investigated in a new UHV CVD/thin film characterization facility in order to determine the reaction mechanism and understand the effect of surface structure on the mechanism. The results show that on a single crystal rutile(100) surface there are parallel reactions to deposit TiO_2: reaction (1) forming propene and water as gas phase products and reaction (2) forming propene and isopropanol. Reaction (1) is favored at higher temperatures (650–800 K) where lower surface coverages of adsorbed isopropoxide ligands favor dehydration, whereas at lower temperatures (550–650 K) the proximity of isopropoxide ligands on the adsorbed TTIP favor a concerted elimination to form propene and isopropanol. At high temperatures (>800 K), the rapid reaction rate forms surface defects which aid in the dehydrogenation of the isopropoxide ligands to form acetone, a process which is more facile on defected polycrystalline surfaces.[16] Thus the single crystal influences which reactions are facile.

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