electrophiles. This inert behavior is consistent with the high deprotonation energy of **3**. The decomposition of **3** was studied in detail by collisional activation and compared with that for ionized **2**. Dramatic differences are observed and are a consequence of low barrier processes for fragmentation of decarbonylated **3**.

We are currently exploring the protonation dynamics of a number of diiron complexes in an effort to further characterize their chemistry with emphasis on comparisons to solution results. These studies will undoubtedly provide new insights into these interesting species.

Acknowledgment is made to the donors of the Petroleum Research Fund, Administered by the American Chemical Society, for support of this Research.

Registry No. **2**, 76722-37-7; **3**, 81616-48-0; **10**, 118599-60-3; **13**, 118599-59-0; C_2D_4, 683-73-8; C_2H_2, 74-86-2; acetaldehyde, 75-07-0; *p*-tolualdehyde, 104-87-0; cinnamaldehyde, 104-55-2; acetone, 67-64-1.

Surface Organometallic Chemistry in the Chemical Vapor Deposition of Aluminum Films Using Triisobutylaluminum: β-Hydride and β-Alkyl Elimination Reactions of Surface Alkyl Intermediates

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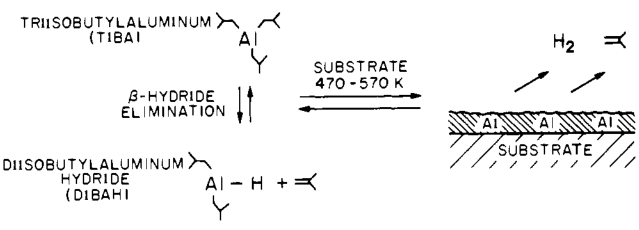
Abstract: Thermal decomposition of triisobutylaluminum (TIBA) to deposit aluminum films shows promise as a way to form conductive contacts on silicon-based electronic devices. An important step in the steady-state deposition is the reaction of TIBA with the growing aluminum surface. We have studied this chemistry by reacting TIBA with single-crystal Al(111) and Al(100) surfaces. A combination of effusive molecular beam scattering, thermal desorption spectroscopy, Auger electron spectroscopy, low-energy electron diffraction, high-resolution electron energy loss spectroscopy, and scanning electron microscopy was used in these studies. We find that TIBA decomposes on both of these aluminum surfaces above ∼470 K by β-hydride elimination reactions to deposit aluminum and evolve hydrogen and isobutylene. This surface β-hydride elimination reaction is the rate-determining step. We find that the reaction is 2–5 times faster on Al(111) than on Al(100). In the temperature range of 470–600 K, the growing film is carbon-free, crystalline, and adopts the orientation of the single-crystal substrate. At higher temperatures, the deposited aluminum contains carbon, and we present evidence that a surface β-methyl elimination reaction is responsible, at least in part, for this contamination. Using the kinetic parameters determined from monolayer thermal deposition experiments for this reaction, we are able to predict the rate of steady-state aluminum deposition for TIBA pressures between 10^{-6} and 1 Torr.

1. Introduction

Of the many sophisticated technologies currently used in electronic materials growth and processing, perhaps none exhibits a richer, more diverse and perplexing range of chemistries than does chemical vapor deposition (CVD).[1] The many advantages of this technique for growing thin films—enhanced conformal coverage, low processing temperatures to name but a few—are well-appreciated. The current literature, which describes commercially significant processes for the growth of oxide, metal, semiconductor, glass, and compound thin-film materials,[2] attests to the broad range of applications that have been developed. At the heart of all of these technologies reside poorly understood patterns of chemical reactivity, namely the adsorption, activation, and transformation of complex gaseous reagents by a solid surface. This is the central focus of the studies reported here.

The system we examine is aluminum film growth by the pyrolysis of triisobutylaluminum (TIBA). We have selected this system for several reasons. First, it is a process that is of significant current interest for the metalization of very large scale integrated (VLSI) devices with feature sizes less than ∼1 μm.[3] Second, the process, as it currently stands, is poorly understood and exhibits complex growth patterns, which may emerge as a direct consequence of fundamental chemical processes occurring on the surface of the substrate.[3,4] Third, and perhaps most significant, this system demonstrates chemical principles that are broadly representative of many CVD systems. As a result, the understanding we develop here may help to suggest approaches by which the relevant features of other systems might be explored.

Scheme I



Putting these generalities aside for the moment, it would be useful to discuss specific issues of interest in this aluminum CVD system. Ziegler and co-workers reported in 1960 that triisobutylaluminum can be pyrolyzed at ∼525 K to deposit aluminum films.[5] By analysis of the gas-phase products (primarily iso-

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(4) Green, M. L.; Levy, R. A.; Nuzzo, R. G.; Coleman, E. *Thin Solid Films* **1984**, *114*, 367. Levy, R. A.; Green, M. L.; Gallagher, P. K. *J. Electrochem. Soc.* **1984**, *131*, 2175.

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butylene and hydrogen) several qualitative aspects of the reaction mechanism were established (Scheme I). The dominant reaction channel they observed is the now familiar β-hydride elimination pathway. It was noted that the first β-hydride elimination step, yielding diisobutylaluminum hydride (DIBAH), occurs at least in part in a facile gas-phase reaction at these temperatures.[6] The subsequent steps leading to metal deposition were unclear and showed several experimental peculiarities. The most significant of these was the observation that the exhaustive thermolysis exhibits autocatalytic behavior in the presence of aluminum metal. How the solid surfaces present in these experiments initiated the growth of metal and how the growing metal film effectively catalyzed this process were unclear. The detailed metallurgy of the deposits formed, as regards crystallinity and orientation, was also not described.

To address these questions, we initiated this study of the surface chemical reactions involved in the chemical vapor deposition of aluminum using TIBA. To isolate the intrinsic surface organometallic chemistry of TIBA from other experimental variables such as gas-phase reactions, a temperature- and pressure-controlled effusive molecular beam of TIBA was directed onto single-crystal substrates in a specially-designed ultrahigh-vacuum (UHV) chamber. Scattered and thermally desorbed products were detected with a mass spectrometer, while low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to determine the surface atomic order and composition.

Using this apparatus, we have previously found that TIBA at room temperature has a very low reaction probability with clean and oxidized single-crystal silicon substrates heated to typical deposition temperatures of 550 K.[7] In contrast, clean aluminum surfaces held at 550 K readily decompose TIBA to deposit aluminum.[8] We report here studies of the surface reaction mechanism for deposition of aluminum from TIBA on clean Al(111) and Al(100) single-crystal surfaces. We find that the organometallic chemistry of TIBA on aluminum surfaces is very similar to the gas-phase and solution chemistry of aluminum alkyls. In the temperature range of 450–570 K, the isobutyl ligands are removed from TIBA to deposit carbon-free, crystalline aluminum films by a surface β-hydride elimination reaction. This process is further characterized by the striking observation that, in the surface decomposition, the three isobutyl groups from the parent TIBA are kinetically indistinguishable, suggesting that adsorption is followed by a facile dissociation of the adsorbate to yield surface alkyl groups. At temperatures greater than 600 K, carbon is incorporated into the growing film, by a process that is believed to involve a surface β-methyl elimination reaction. The rate of the surface β-hydride elimination reaction is 2–5 times faster on Al(111) than on Al(100) between 570 and 470 K. Finally, the kinetic parameters for this reaction, which were determined from monolayer thermal desorption experiments, are utilized in a simple model to accurately predict the rate of steady-state aluminum CVD for TIBA pressures between 10^{-6} and 1 Torr.

2. Experimental Section

Experiments were carried out in two diffusion-pumped UHV chambers ($P \leq 10^{-10}$ Torr) each equipped with AES (single-pass CMA), four-grid LEED optics, a differentially pumped quadrupole mass spectrometer (0–300 amu), ion sputtering gun, and an effusive molecular beam doser. One of the chambers was also equipped with a high-resolution electron energy loss spectrometer (EELS) for surface vibrational spectroscopy. This EELS chamber and spectrometer have been described previously.[9] Relevant aspects of the other UHV system, in which the TIBA scattering and thermal desorption experiments were performed, will be described here.

The effusive molecular beam doser is a 3.2-mm-diameter stainless steel tube capped by a Ni disk bearing a 200-μm pinhole. The tube is wrapped with insulated nichrome wire and can be resistively heated to over 500 K. During the experiments described below, the doser and gas handling lines were maintained at 330–350 K to avoid TIBA condensation. The pressure behind the doser pinhole was monitored with a bakeable capacitance manometer (MKS, 1-Torr full scale). The pressure was controlled dynamically by continuously pumping on the source while varying the source temperature. The gas handling line is equipped with a catalytic cracker heated to >550 K to decompose this pyrophoric aluminum alkyl before it enters the pump. We found that it was necessary to condition both the doser and the gas handling line for several hours with TIBA after each exposure to air before a consistent TIBA mass spectrum could be obtained. The characteristic cracking fragments for TIBA in our mass spectrometer with an electron ionization energy of 70 eV are (intensities relative to m/e = 85 are in parentheses) 85 (1), 99 (0.09), 141 (0.35), and 198 (0.05) along with fragments at m/e = 56 and below for the isobutyl ligands. This cracking pattern is consistent with unpublished Fourier transform mass spectra of this compound.[10] The intensity of the isobutyl fragments relative to m/e = 85 varies due to differing amounts of isobutylene entering the chamber along with TIBA (note that TIBA is always in equilibrium with isobutylene and DIBAH as shown in Scheme I). Since isobutylene does not react with aluminum surfaces between 150 and 700 K (as shown in section 3.3), this contamination was not viewed as being a problem that complicates the interpretation of the studies reported herein. DIBAH produced in the equilibrium with TIBA has a low vapor pressure,[11] and, as shown in section 3.1, there is no evidence for DIBAH in mass spectra of the flux from the effusive source.

Two Al(111) and three Al(100) single-crystal samples were used in these experiments. All samples were about 0.5 cm^2 by 2 mm thick. The aluminum crystals were cut by spark erosion from oriented single-crystal boules (99.9999%, Johnson Matthey Chemicals, Ltd.), reoriented by Laue back-diffraction to within 1° of the desired angle (except for one nominally (111) Al crystal, which was used as cut), and mechanically polished with 600-grit sand paper followed by 5.0-, 1.0-, and 0.3-μm alumina polishing compounds (Buehler Ltd.). Highly reflective, but not mirror finish,[12] surfaces were obtained by polishing for about 5 min with each compound in 4 M ammonium hydroxide solutions. All samples were mounted on molybdenum heater stages using small Ta tabs spot-welded to the heater and bent over the edges of the crystals. These heaters were in turn connected via a copper braid to a liquid-nitrogen reservoir for temperature control from 100 to 1300 K. Chromel–alumel thermocouples (0.25-mm wires) were used to monitor sample temperature. For the nominal (111) aluminum crystal, the thermocouple was spot welded to one of the Ta tabs. For all other samples, the thermocouple wires were spot welded together and wedged into a 0.5-mm hole spark-eroded into the side of the crystal in order to more accurately monitor the surface temperature.

Samples were cleaned in situ by cycles of sputtering with 1-kV Ar$^+$ or Ne$^+$ ions at 600 K and annealing in UHV at 700–750 K. Initial cleaning of the aluminum crystal required many hours of sputtering to remove all traces of aluminum oxide (due to alumina polishing compound embedded in the sample) from the near surface region. Despite this extensive sputtering and the somewhat greyish to frosty appearance of the surface, the clean and annealed aluminum single-crystal surfaces showed sharp (1 × 1) LEED patterns. Scanning electron micrographs of the single-crystal samples after depositions were taken on a Cambridge Laboratories 25-keV scanning electron microscope. Samples were transferred from the vacuum chamber to the microscope in air with no special precautions. A thin native oxide overlayer forms on the sample when it is handled in this manner, but the resulting changes in the surface morphology are beneath the resolution limit of the SEM.

In most of the steady-state scattering experiments reported below, the effusive TIBA beam was incident on the surfaces at 20–30° from the normal and scattered into the mass spectrometer fixed at approximately the specular direction. The mass spectrometer was fitted with a skimmer having a 3-mm-diameter hole. The sample was held about 1 cm from both the mass spectrometer skimmer and the effusive beam source. In the scattering experiments of Figure 12, the aluminum crystals were held directly in front of the mass spectrometer about 1 mm from the skimmer. This arrangement lowered the incident TIBA flux by approximately a

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(10) Reents, W. D., private communication.

(11) At 373 K, the vapor pressure of DIBAH (which is a trimer in solution) is 0.3 Torr compared to 16 Torr for TIBA (technical data sheets from Ethyl Corp.). Therefore, for a DIBAH/TIBA mixture that is *90% DIBAH*, 85% of the vapor at 373 K will be TIBA assuming ideal solution behavior: Berry, S. R.; Rice, S. A.; Ross, J. *Physical Chemistry*; Wiley: New York, 1980; p 912.

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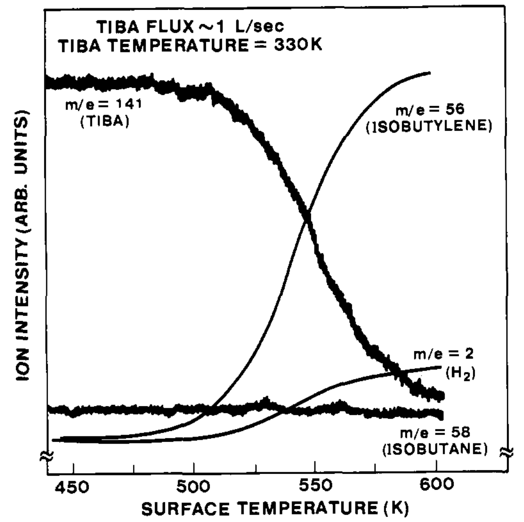

Figure 1. Scattered species as a function of surface temperature when TIBA (T_{gas} = 330 K) is impinged onto an Al(100) surface at an effective pressure of 10^{-6} Torr. The surface temperature is ramped linearly at ~2 K/s, and the mass profiles are approximately reversible (see text). The arbitrary units are different for each of the scattered fragments, which prohibits comparison of their relative intensities.

factor of 20 but ensured that only those species scattered from the center of the single-crystal surface were detected. The only scattered species whose intensity profile as a function of surface temperature proved to be substantially different in the two configurations was *m*/*e* = 198, the TIBA molecular ion. When the crystal was held within 2 mm of the skimmer, the molecular ion had the same intensity vs surface temperature profile as its cracking fragments *m*/*e* = 141 and 85. However, when the crystal was held further from the skimmer, the crystal supports were imaged and the intensity of *m*/*e* = 198 decreased at lower temperatures than for the cracking fragments, strongly suggesting that TIBA was being converted on the crystal supports to DIBAH whose cracking pattern contains both *m*/*e* = 141 and 85 but no *m*/*e* = 198.

In the thermal desorption experiments, the samples were held about 1 mm from the mass spectrometer skimmer. TIBA dosing was done with the effusive molecular beam doser. Hydrogen atoms were adsorbed onto the aluminum surfaces by evaporating them from a hot tungsten filament. The filament (0.22-mm W wire) was held about 0.5 cm from the aluminum surface and heated to ~2000 K with 1.8-A current while back-filling the chamber with hydrogen. All other gases were adsorbed by back-filling the chamber.

Reagents were obtained from the following sources: Ar, Matheson (99.995%); Ne, Matheson (99.995%); hydrogen, Matheson (99.995%); deuterium, Matheson (99.5 atom %); isobutylene, Matheson (research purity, 99.9%); triisobutylaluminum, Ethyl Corp. (>95%) and Alpha Products (95.7% and 99.99%). The head gas over the TIBA source was purified before each use by pumping on the cylinder while heating it to 330–370 K; this procedure was employed until a constant mass spectrum was obtained. Hydrogen and deuterium were passed through a catalytic purifier before introduction into the chamber. Argon, neon, and isobutylene were used as received.

3. Results and Interpretation

We present and interpret our results in three parts. In the first, we describe the steady-state scattering of TIBA from the various aluminum surfaces. Next, we examine the morphology of film growth. Finally, we detail the results and significance of monolayer adsorption experiments. In each section, the results for Al(100) will be presented first, followed by a comparison with the chemistry observed on Al(111).

3.1. Steady-State Scattering of Triisobutylaluminum. Figure 1 shows how the intensities of ions derived from scattered and desorbed reactants and products vary with surface temperature when an effusive beam of TIBA (T_{gas} = 330 K) is impinged onto an Al(100) surface. The surface temperature was ramped linearly at ~2 K/s, and the flux of incident TIBA corresponds to an effective pressure of ~10^{-6} Torr at the crystal surface. We see from Figure 1 that the scattered flux of *m*/*e* = 141 (a cracking fragment of reactant TIBA) decreases while the scattered fluxes of product isobutylene (*m*/*e* = 56) and hydrogen (*m*/*e* = 2) increase between 500 and 600 K, the typical CVD temperature range. The curves level out above 600 K, indicating the onset of a kinetic regime in which the flux of the reactant to the surface is rate-limiting. The absolute ion intensities, which are indicative of increases or decreases in the various scattered species, are in arbitrary units and thus cannot be compared in a simple manner. We note, however, that when *m*/*e* = 198, 141, and 85 (TIBA molecular ion and two cracking fragments) are set to the same initial mass spectrometer intensity, they produce superimposable curves as a function of surface temperature.[13] This result indicates that there is little if any DIBAH, which has a molecular ion of *m*/*e* = 141 and *m*/*e* = 85 as a cracking fragment, in the incident flux of TIBA.[11]

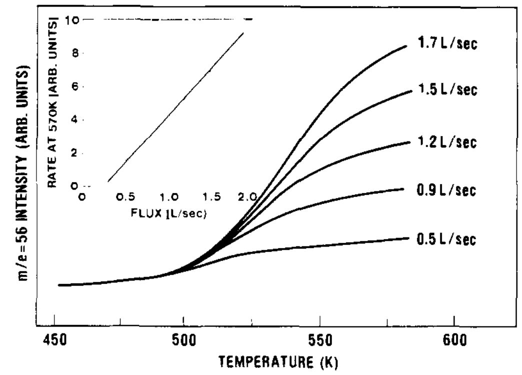

Figure 2. Isobutylene evolution from Al(100) as a function of incident TIBA flux and surface temperature. For these fluxes of <2 langmuir/s the rate of isobutylene production is independent of flux below 500 K and approximately first-order in TIBA flux at 570 K as shown in the inset.

Masses corresponding to potential products other than isobutylene and hydrogen were also monitored. We looked in particular for isobutyl radical and isobutane being formed as desorption products. Our results conclusively demonstrate that significant quantities of isobutane are not produced under the experimental conditions outlined in Figure 1 (as shown by the lack of increase in *m*/*e* = 58 with increasing surface temperature). There is, however, some intensity for *m*/*e* = 57, which at the levels observed can be attributed completely to the M + 1 ion of isobutylene. We further conclude that heavier (polymerized) hydrocarbon products are probably not produced judging from the lack of an increase in the *m*/*e* = 99 ion, a likely cracking fragment for dimerized isobutyl species.[14] The evolution of hydrocarbons with fewer than four carbons could not be assessed because of the very strong interference from the isobutylene cracking fragments.

The profiles of scattered species in Figure 1 are reasonably reversible, in that they may be traced repeatedly from low to high temperature and visa versa with little hysteresis.[15] Auger electron spectroscopy shows that the surface remains free of carbon, and LEED shows that the Al(100) (1 × 1) structure is maintained throughout. These results indicate that high-purity, crystalline aluminum can be deposited on an Al(100) surface from TIBA *without* prior gas-phase conversion to DIBAH. We also note that,

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(13) This result could only be obtained when the crystal surface was placed within ~2 mm of the mass spectrometer skimmer. At larger distances from the skimmer, the crystal supports were imaged, and while all three fragments still showed the same overall percentage decrease, the profile for *m*/*e* = 198 was different that that for either *m*/*e* = 141 or *m*/*e* = 85 (see the Experimental Section).

(14) *m*/*e* = 99 actually decreases over the temperature range of 500–600 K, since it is also a cracking fragment of TIBA. Dimerization of two isobutyl groups to give 2,5-dimethylhexane, therefore, cannot be completely ruled out by this experiment.

(15) The hysteresis is only evident in the high-temperature portion of the curves. In this region, on cooling, such reaction products as *m*/*e* = 56 decrease more rapidly (by ~20% of the total signal) than one would predict from the heating curves while such reactants as *m*/*e* = 141 increase more slowly than one would predict from the heating curves. These effects can be attributed both to depletion of the local background concentration of TIBA during the heating cycle and to an increase in the amount of TIBA adsorbed onto the surface during the cooling cycle.

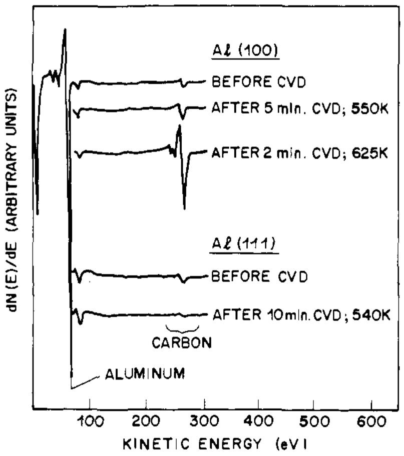

Figure 3. Auger electron spectra before and after chemical vapor deposition (CVD) of aluminum using TIBA on Al(100) (top) and Al(111) (bottom) surfaces at the indicated temperatures. As discussed in the text, these spectra show that high-purity aluminum films are deposited at surface temperatures less than 600 K, while carbon is incorporated in the growing aluminum film for deposition temperatures >600 K.

since the deposition products (isobutylene and hydrogen) are the same as those observed in aluminum deposition from TIBA at ~1 Torr,[5] it appears that the same surface chemistry is controlling the aluminum deposition at 10^{-6} Torr and at 1 Torr.

The pressure dependence of the deposition on Al(100) was investigated as a function of surface temperature. These results are shown in Figure 2. For TIBA fluxes of 0–2 langmuir/s (1 Langmuir = 10^{-6} Torr·s) the deposition rate varies from being independent of TIBA flux at low temperatures to approximately first order in TIBA at 570 K as shown in the inset. The nonzero intercept in the pressure dependence at 570 K is due, we believe, to a systematic error in the pressure measurement.[16]

A test of the reversibility of the surface decomposition reaction can be made, in principle, by examining isotope-exchange patterns. With this in mind, we have examined isotope exchange during the CVD reactions by exposing an Al(100) crystal to a background pressure of 1×10^{-6} Torr of deuterium while scattering a comparable flux of TIBA off the surface. Masses 3, 30, 58, and 60 were monitored as a function of surface temperature to check for deuterium incorporation into the decomposition products (isobutylene and hydrogen). None was observed. This observation cannot be interpreted conclusively, however, in as much as hydrogen dissociation on clean aluminum surfaces exhibits a reasonable activation barrier.[17,18]

One of the more significant results described above is that aluminum deposition carried out at temperatures below 570 K resulted in the formation of carbon-free films. In stark contrast, TIBA pyrolysis on Al(100) above 600 K resulted in significant carbon contamination of the deposited layer. This is illustrated by the AES spectra shown in Figure 3. The top portion of the figure shows the results for growth on an Al(100) crystal while the lower portion is for an Al(111) surface. These two sets of data were acquired in different chambers, which differed dramatically in the quantities of TIBA that had been dosed into the system. The Al(100) data were obtained in the principal ultrahigh-vacuum apparatus used in this study. Control experiments indicate that as a result of the routine TIBA exposures in this system some carbon contamination of the aluminum surface inevitably occurred during AES as a result of the unavoidable outgassing of the spectrometer filament. The top trace shows the level of carbon contamination on the Al(100) surface before CVD. The second trace shows the surface composition after scattering TIBA at an effective pressure of 1.5×10^{-5} Torr and a surface temperature of 550 K for 5 min. We estimate (see section 4.3) that at least 15 layers of aluminum have been deposited during this experiment. The slight increase in intensity of the peak at 272 eV can be attributed to carbon *on the surface* of the Al crystal (see above). By contrast, after 2 min of TIBA scattering at 625 K to deposit at least 35 layers of aluminum, there is significant carbon contamination of the film, and a carbide AES line shape is observed (as shown in the third spectrum of Figure 3).[19] Using reported AES sensitivities for carbon and aluminum,[20] we calculate that the aluminum deposited at 625 K is contaminated with ~33 atom % carbon. The bottom portion of Figure 3 shows the results for growth on an Al(111) single-crystal surface in the "cleaner" UHV chamber. In this experiment, films comparable in thickness to those above were grown on the substrate. The significant feature to note is that when care is taken to avoid carbon contamination due to filament outgassing, extremely clean surfaces are found for growth in the lower temperature regime. A striking example of this purity is shown in the lower trace where the level of carbon in the near surface region after deposition is *less* than before.

The results obtained for TIBA scattering from an Al(111) surface proved in most respects to be analogous to those observed for Al(100): isobutylene and hydrogen are the scattered products, the aluminum film grows with a (111) orientation (as determined by LEED), and the deposited aluminum is carbon-free (by AES) at growth temperatures less than 570 K, while extensive carbon incorporation is observed at deposition temperatures >620 K. A closer examination of the data, however, reveals a significant difference between Al(111) and Al(100), namely that the aluminum deposition rate is substantially faster on the (111) surface. This difference in rates will be quantified with the results from monolayer thermal desorption experiments in section 3.3.

3.2. Surface Morphology. Throughout these studies of the chemical vapor deposition of aluminum on the (111) and (100) faces of aluminum single crystals, the (1 × 1) LEED patterns of these surfaces were maintained. Therefore, we conclude that the aluminum film grows epitaxially on both the (111) and (100) surfaces. In the case of the (111) surface, the 3-fold symmetry of the LEED spot intensities was also maintained, indicating a continuation of the abc layer packing in the growing aluminum film.[21] This epitaxial growth was observed throughout the temperature range of 510–640 K for both Al(111) and Al(100), a surprising result given the extensive carbon contamination that occurs at temperatures above 600 K. Depositions of up to 0.1 μM of aluminum (thickness based on calculations presented in section 4.3) were carried out on both substrates without loss of crystallinity.

The CVD aluminum films grown on these single-crystal aluminum surfaces were reflective, albeit somewhat greyish to frosty in color, reflecting the appearance of the original substrate after the many cycles of ion sputtering and annealing necessary to remove the embedded aluminum oxide polishing compound (see the Experimental Section). As a result, the variety of topographies observed in SEM studies may largely reflect the initial substrate topology after cleaning. In general, however, micron-size crystallites were observed such as those shown in parts A and D of Figure 4 for growth on Al(100) and Al(111) surfaces, respectively. The (100) or (111) nature of the crystallites is evident from their shape. These particular CVD aluminum films were deposited above 600 K. On films grown at lower temperatures, the crystallite

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(16) Note from Scheme I that TIBA is always in equilibrium with DIBAH and isobutylene, so that the total measured pressure will be greater than the actual partial pressure of TIBA.

(17) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H., unpublished results.

(18) Paul, J.; Hoffmann, F. M. *Surf. Sci.* **1988**, *194*, 419. Paul, J., submitted for publication in *Phys. Rev. B*.

(19) While approximately $2^1/_2$ times as much aluminum was deposited at 625 K as at 550 K, both the >6-fold increase in the 272-eV carbon peak-to-peak height and the carbide line shape after CVD at 625 K are strong evidence for carbon incorporation *into* the growing aluminum film.

(20) Mroczkowski, S.; Lichtman, D. *J. Vac. Sci. Technol., A* **1985**, *3*, 1860.

(21) Crystalline aluminum has a face-centered-cubic lattice, so the (111) surface LEED pattern shows 3-fold symmetry in the spot intensities reflecting the abc layer packing. The aluminum deposited by CVD could potentially grow with an abab layer packing to give a hexagonal-close-packed lattice. The close-packed face of such a lattice would have a 6-fold symmetry in the intensities of the LEED spots that is not observed. For a discussion of this method of analysis, see: Ertl, G.; Küppers, J. *Low Energy Electrons and Surface Chemistry*, 2nd ed.; VCH: Deerfield Beach, FL, 1985; p 201–266.

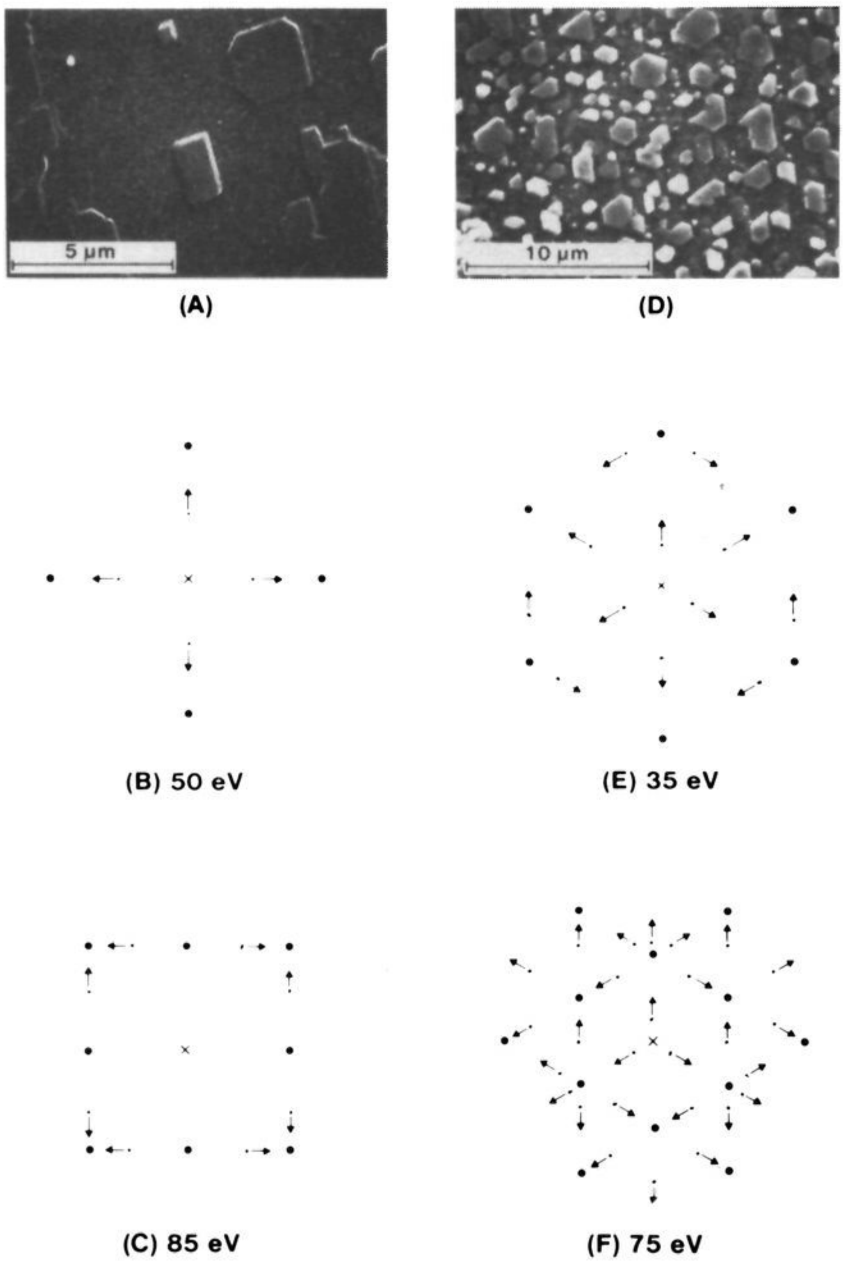

Figure 4. Scanning electron micrographs of the surface morphology and schematic diagrams of the low-energy electron diffraction patterns observed after CVD of ~100 nm of aluminum at 650 K on Al(111) and Al(100) single-crystal substrates. A and D are micrographs of the Al(100) and Al(111) surfaces, respectively. B and C are the LEED patterns for Al(100) while E and F are the LEED patterns for Al(111) at the indicated electron beam energies. The arrows show the direction in which the small (facet) spots move with increasing beam energy. These spots are attributed to the edge planes of the crystallites observed in the micrographs.

edges generally were not as well-defined. We have observed that the topographies that characterize samples grown in this low-temperature regime are not as complex, tending mostly toward smoother, less faceted surfaces. The relevant aspects in the high-temperature regime—be they carbon segregation or flux-limited growth effects—are unclear to us at present. The salient point remains, however, that epitaxy and simple morphologies can be obtained in this CVD system. The complex structures typically obtained in commercial reactors are not intrinsic to the chemistry of TIBA pyrolysis.

While all of these CVD films showed (1 × 1) LEED patterns at room temperature, additional LEED spots were evident on both the (111) and (100) surfaces upon cooling. These additional spots were generally faint, but sharp, and moved in directions away from the (0, 0) spot with increasing electron beam energy as shown schematically for several beam energies in the lower portion of Figure 4. These extra spots can be reasonably attributed to edge planes (facets) of the crystallites observed in the SEM photos of parts A and D of Figure 4.[22]

3.3. Monolayer Adsorption Experiments. Thermal desorption experiments confirmed the high reactivity of TIBA on clean aluminum surfaces. When TIBA is condensed in submonolayer quantities on an aluminum surface held at 150 K and the surface is subsequently heated, decomposition and not molecular desorption is observed. Within the limits of detection, all of the adsorbed TIBA decomposes to produce isobutylene and hydrogen.[23] The generality of this result is illustrated in Figure 5, which shows thermal desorption data for an Al(100) surface exposed to varying amounts of TIBA at 200 K. The thermal desorption spectra in Figure 5 show that both isobutylene and hydrogen are evolved with a peak temperature of ~520 K, consistent with the steady-state CVD observed at this temperature. The peak at 205 K in the isobutylene spectra for a 5-langmuir exposure of TIBA is a cracking fragment from molecular desorption of TIBA condensed in a second layer. All of the thermal desorption experiments in Figure 5 were reproducible and *did not* require surface cleaning between runs, consistent with AES spectra, which showed that the cycle of adsorption and decomposition of TIBA yields clean surfaces. In addition, low-energy electron diffraction showed a (1 × 1) diffraction pattern after each of these experiments, and *no new diffraction patterns were observed during adsorption of TIBA* on the surface.

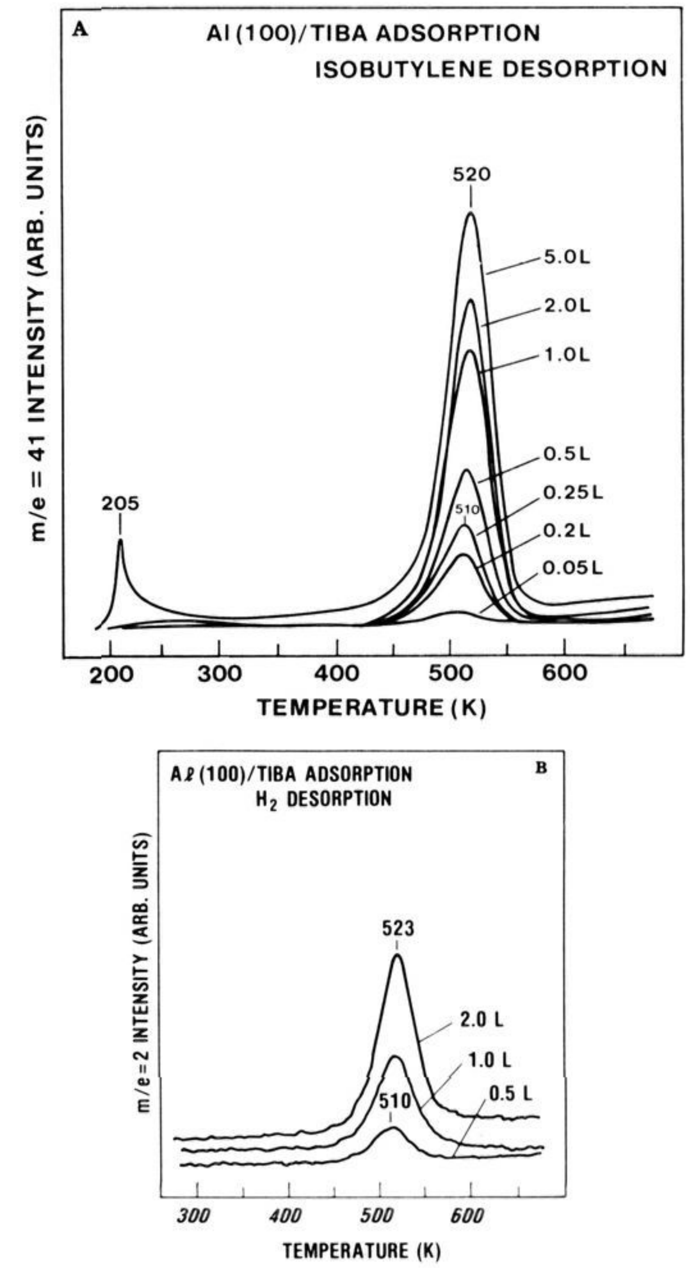

Figure 5. (A) Isobutylene and (B) hydrogen desorption from an Al(100) surface as a function of TIBA dose at ~200 and ~275 K, respectively. The surface heating rates are 6.5 and 7.5 K/s, respectively. A (1 × 1) LEED pattern is maintained throughout these experiments, and AES shows that the surfaces are free from carbon contamination after each thermal desorption.

To determine whether hydrogen or isobutylene desorption exhibits kinetic competence as a possible rate-limiting step in the thermal desorption spectra of Figure 5, we studied their adsorption on an Al(100) surface. We found that isobutylene interacts

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[22] Judging from the energies at which the facet spots pass through the (0,0) beam, the edge planes on the crystallites of the (100) surface appear to be (111) facets.

[23] Small amounts (over an order of magnitude less than isobutylene) of m/e = 141 and 85 are observed to desorb with a peak temperature of ~480 K. Judging from the absence of any m/e = 198 desorption, these fragments are probably due to DIBAH (MW = 142) rather than to TIBA (MW = 198). We have yet to determine if this DIBAH results from TIBA decomposition or rather is coadsorbed as a contaminant.

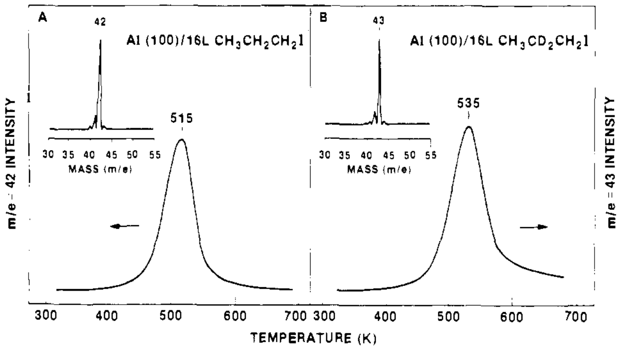

Figure 6. TPD and IDMS[26] data showing propylene desorption derived from the adsorption and thermal decomposition of propyl iodide on an Al(100) surface. In A, the adsorbate used is 1-iodopropane while in B 1-iodopropane-*2,2*-d_2 was used. An exposure of 16 langmuir was used in each with a heating rate of 10 K/s.

weakly, desorbing molecularly from Al(100) at 130 K. At higher temperatures (up to 700 K), we were unable to chemisorb isobutylene on Al(100) even for exposures >1000 langmuir, suggesting that a significant barrier exists for any dissociative adsorption pathways. We also found that an Al(100) surface does not dissociatively chemisorb hydrogen with any facility. To overcome this barrier to H_2 dissociation and to study H atoms on the aluminum surface, a tungsten filament was used to atomize H_2 and to dose H atoms directly onto an Al(100) surface held at 120 K.[17,18] Thermal desorption of H_2 from these atomic hydrogen monolayers occurred with a peak temperature of ~330 K.[24] Since *both isobutylene and hydrogen desorb from Al(100) below 350 K*, the simplest conclusion we can draw is that *their production from TIBA at 520 K must be limited by the rate of some other elementary step.* Our belief (as elaborated in section 4.1) is that this process is a surface β-hydride elimination reaction.

The observation of only one peak for isobutylene evolution in the thermal desorption spectra of Figure 5 (and its close similarity to the TPD data in Figure 6, see below) implicitly establishes the most remarkable feature about this reaction, namely that all three isobutyl groups derived from the TIBA adsorbate behave in a manner in which they are kinetically indistinguishable. We defer further comment on this important point to the Discussion.

Additional insight into the nature of the surface β-hydride elimination implicated above can be obtained, in principle, by preparing comparable surface alkyl intermediates by an independent synthetic route. The attraction of such a study resides not only in its ability to model the adsorbed species derived from TIBA but in the potential it offers to isolate their decomposition kinetics from that which must certainly characterize a reasonably complex adsorption process. Toward this end we have found a suitable synthetic protocol. We have observed that most alkyl iodides, especially those with linear and branched alkyl chains of three carbon atoms or more, are dissociatively chemisorbed on Al(111) and Al(100) to give a high density of surface alkyl groups.[25] The reactive adsorption process is very efficient; cleavage of the C–I bond appears to occur at low temperatures (<200 K). The most significant finding to note here, however, is that the thermal chemistry of these surface alkyl groups is largely unperturbed by the coadsorbed iodine atoms.

Figure 6 presents a specific example that illustrates the mechanistically simple character of β-hydride eliminations occurring on aluminum surfaces. Shown in the figure are TPD and integrated desorption mass spectral (IDMS)[26] data for two propyl iodides (which contain hydrogen atoms in the β-positions) chemisorbed on Al(100). The second part of the figure differs from the first in that the adsorbate used is the specifically labeled isomer 1-iodopropane-*2,2*-d_2. Several significant features are apparent in the data. First, the desorbed product is exclusively propylene. Second, the TPD data show line shapes and peak maxima analogous to that in the high-temperature portion in Figure 5, suggesting *strong similarities* in the chemistries that yield propylene in the present case and isobutylene in the latter. Third, the IDMS data, obtained with a 15-eV ionizer energy so as to emphasize primarily the molecular ion, show that the labeled propylene is d_1, strongly suggesting that the β-hydride elimination is irreversible. Fourth, as judged by the TPD peak maxima, the desorption process shows a pronounced kinetic isotope effect.[27] From the brief discussion above, there seems little doubt that β-hydride elimination reactions of alkyl groups chemisorbed on aluminum surfaces can occur with kinetics comparable to that which characterizes the rate-determining step in TIBA decomposition.

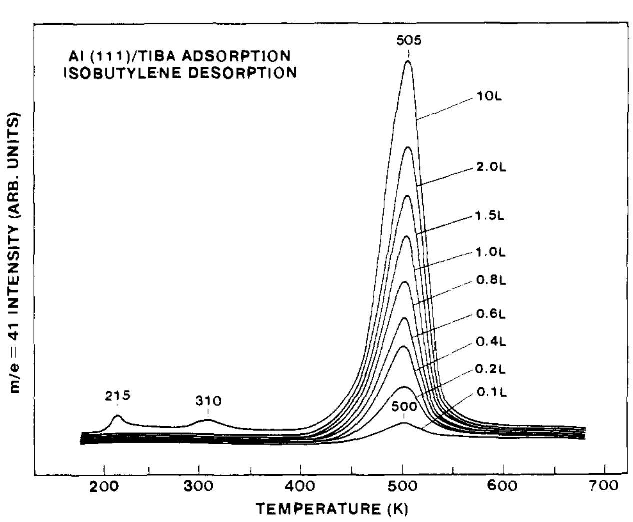

Figure 7. Isobutylene desorption from an Al(111) surface as a function of TIBA dose below 200 K. The surface heating rate is 7 K/s.

To further study the reversibility of this β-hydride elimination step, we examined the chemistry of isobutylene coadsorbed with H atoms on Al(100). First, H atoms (half the amount of a saturation exposure) were adsorbed onto an Al(100) surface held at 100 K. A total of 1 langmuir of isobutylene was subsequently adsorbed. When the surface was heated, isobutylene desorbed at ~130 K and hydrogen at ~300 K. There was no evidence for formation of isobutyl groups judging from the lack of isobutylene and hydrogen desorption at ~500 K (the temperature at which they are produced from the isobutyl groups in TIBA). This result strongly suggests that the microscopic reverse process of β-hydride elimination, olefin insertion into a surface Al–H bond, is irreversible under the conditions employed in this study.

We have determined the activation energy for the production of isobutylene from TIBA on Al(100) by measuring the shift in the thermal desorption peak temperature as a function of the surface heating rate. Using a saturation exposure of TIBA and varying the surface heating rate from 1.5 to 16 K/s (peak temperature shift of 38 K), we find an activation energy of 32.6 kcal/mol using the analysis of Redhead.[28] The corresponding preexponential factor similarly determined is 1.4×10^{13} s^{-1}. While this analysis is not correct in any rigorous sense, since it assumes a coverage independence of both kinetic parameters,[29] we show in the Discussion that these parameters do, in fact, provide a good fit to the steady-state CVD data.

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(24) This desorption temperature is consistent with the results of J. Paul.[18]

(25) Bent, B. E.; Zegarski, B. R.; Dubois, L. H.; Nuzzo, R. G., to be submitted for publication.

(26) This high-sensitivity method collects a complete mass spectrum integrated across a desorption feature. See: Dubois, L. H. *Rev. Sci. Instrum.*, in press.

(27) If one assumes that the ratio of preexponential terms, A_H/A_D, is unity, the difference in peak maxima temperatures yields a difference in activation energies of ~1 kcal/mol. This suggests a kinetic isotope effect, k_H/k_D, of ~2.6 at 520 K. The assumption that $A_H/A_D \sim 1$ may in fact be a poor one, however. See: Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980.

(28) Redhead, P. A. *Vacuum* **1962**, *12*, 203.

(29) For a first-order desorption process the shift in the peak temperature with coverage implies that the desorption parameters change with coverage.[28] The shift observed in Figure 5A is, however, quite small.

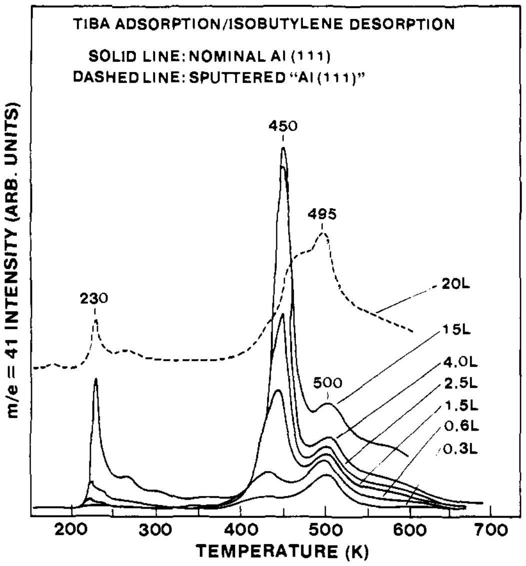

Figure 8. Isobutylene desorption from a nominally (111) aluminum surface (solid lines) and its sputtered counterpart (dashed line) after the indicated TIBA doses at <200 K. The heating rate is 6 K/s. As discussed in the text, the thermocouple was not directly attached to the single-crystal surface for these experiments, so the absolute temperatures are inaccurate.

Similar behaviors and results were found in thermal desorption studies on Al(111) (see Figure 7). These spectra are quite similar to those presented in Figure 5 for studies on Al(100), with the exception that the peak temperature is ~15 K lower, consistent with the faster rate of steady-state CVD on Al(111), which is in fact observed experimentally (see below). The peak at 215 K for the 10-langmuir exposure is due to a TIBA cracking filament, reflecting desorption from a multilayer, while the small peak at 310 K remains unidentified. As was done for Al(100), we measured the shift in the isobutylene desorption peak temperature, which occurs upon variation of the surface heating rate, in order to determine the kinetic parameters for the surface reaction. Using a saturation coverage of TIBA and varying the heating rate from 1 to 20 K/s (peak temperature shift of 40 K), we obtained an activation energy of 27.7 kcal/mol and a preexponential factor of 3.8×10^{11} s^{-1}, values substantially different from those found for Al(100). The correlation between these thermal desorption kinetic parameters and the steady-state CVD rates will be quantified in the Discussion.

Several additional insights into the mechanism of TIBA decomposition on aluminum surfaces were obtained from thermal desorption studies with an aluminum single crystal of nominally (111) orientation.[30] Figure 8 shows isobutylene thermal desorption spectra after TIBA adsorption on this surface. The solid curves are spectra obtained as a function of TIBA exposure to the clean and annealed surface, while the dashed curve shows the effect that sputtering this surface had on the saturation exposure spectrum. Since the temperature measurement in these spectra was recorded with a thermocouple spot-welded to the crystal supports rather than inserted into the side of the crystal, the temperatures reported here are inaccurate and cannot be directly compared to those presented above in Figure 7 for the Al(111) surface. With this reservation aside, it is evident that two peaks (450 and 500 K) are observed as opposed to the single peak, which characterizes adsorption and decomposition on the well-oriented Al(111) surface.

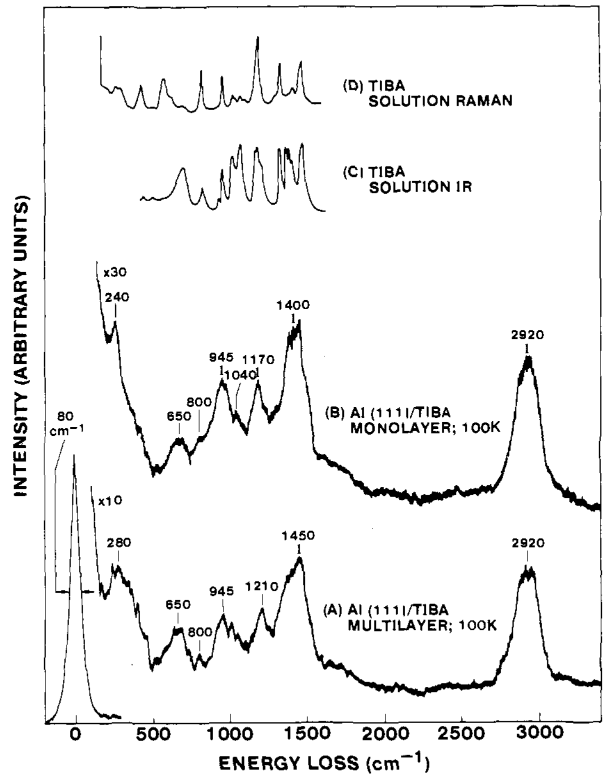

Figure 9. Specular high-resolution electron energy loss surface vibrational spectra of (A) multilayers of TIBA and (B) a monolayer of TIBA adsorbed on Al(111) at 100 K. For comparison, portions of the solution infrared and Raman spectra for TIBA are included as C and D.[32]

We see from the dashed curve that sputtering the surface increases the intensity of the higher temperature shoulder. As a result, we attribute the 500 K peak to surface imperfections and the one at 450 K to (111) terraces. It is interesting to note that the imperfections have a slower rate of isobutylene production as compared to the (111) terraces, analogous to the slower rate observed on Al(100) (Figure 5). The solid lines in Figure 8, showing isobutylene desorption as a function of TIBA exposure, provide evidence for diffusion of the isobutyl ligands on the surface. For low exposures of TIBA, the higher temperature peak (500 K) associated with surface imperfections is dominant, despite its being due to minority sites on the surface. This result implicates diffusion of the isobutyl ligands (with or without their attached aluminum atom) to these surface sites below the temperature at which the β-hydride elimination occurs. Since the peak associated with the population of these imperfections occurs at a higher temperature than that for decomposition on the (111) terraces, the isobutyl ligands must be more strongly bound at these defect sites.[31]

Surface vibrational spectra of TIBA adsorbed on Al(111) were recorded, but these spectra did not provide substantial insight into the surface bonding of TIBA or reveal at what temperature the isobutyl ligands diffuse away from the aluminum atom to which they were originally attached. These high-resolution electron energy loss surface vibrational spectra are shown in Figure 9, which compares spectra for (A) a multilayer and (B) a monolayer of TIBA to the solution infrared and Raman spectra of this compound.[32] While the resolution of EELS does not permit a definitive assignment of the surface spectra for an adsorbate of this complexity, the general features of the multilayer spectrum are consistent with the infrared and Raman peaks. The monolayer spectrum is also remarkably similar, consistent with and strongly suggestive of the formation of surface isobutyl species. Perhaps the most significant insight from this study comes from our observation that, in the absence of condensed water from the chamber

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(30) This crystal was cut approximately parallel to the end face of a (111)-oriented boule, polished, and inserted into the UHV chamber without confirming its orientation by X-ray diffraction. Subsequent determination of the surface orientation was precluded when the sample was inadvertently melted in the vacuum system.

(31) Even though the isobutyl groups are more strongly bound at the imperfections, it is possible (and not inconsistent with our thermal desorption results) that all of the decomposition to evolve isobutylene and hydrogen occurs on the (111) terraces. For a discussion of such a step/terrace equilibrium, see: Serri, J. A.; Tully, J. C.; Cardillo, M. J. *J. Chem. Phys.* **1983**, *79*, 1530.

(32) Hoffmann, E. G. *Z. Elektrochem.* **1960**, *64*, 616.

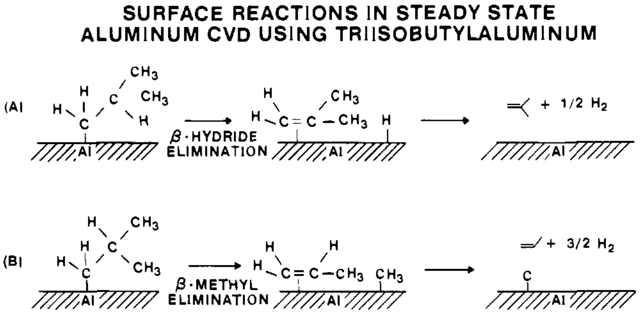

Figure 10. Proposed surface reaction mechanisms for the TIBA ligands on aluminum surfaces during steady-state aluminum CVD. For simplicity, the attached aluminum atom is not shown. The β-hydride elimination reaction (A) dominates at surface temperatures <600 K and leads to carbon-free, crystalline aluminum films. We propose that the β-methyl elimination reaction (B) and subsequent α-hydrogen abstractions from the surface methyl group are the source of carbon incorporation into aluminum films deposited above 600 K.

background gases, the monolayer in Figure 9B *can be annealed to temperatures >400 K without significant spectral changes.* When H_2O contamination is present, heating to 300 K produced an intense mode at ~800 cm^{-1}, which we assign to an AlO_x species.[12] These data, when taken together with the TDS results presented above, indicate that TIBA adsorption results in the formation of a strongly adsorbed surface isobutyl species. It further establishes that this moiety persists on the surface at temperatures greater than that at which either molecular TIBA or isobutylene desorb and surface bound hydrogen atoms combine to evolve H_2 (see above). As we will discuss in detail below, the data is most simply interpreted by assuming that the strong adsorption of TIBA on aluminum involves the dissociation of at least one Al–C bond in the adsorbate. This adsorbed species is also found by EELS to be highly reactive toward H_2O, a characteristic property of aluminum alkyls.

4. Discussion

4.1. Surface Reactions. Our results clearly show that the steady-state deposition of aluminum from TIBA requires no prior gas-phase conversion of the metal alkyl to diisobutylaluminum hydride. Clean Al(111) and Al(100) surfaces readily effect the decomposition of TIBA in the temperature range of 450–600 K to deposit atomically pure aluminum films while evolving isobutylene and hydrogen. These products are consistent with a surface β-hydride elimination reaction by the isobutyl ligands as illustrated in Figure 10A. Such a reaction is well-documented for TIBA in the gas phase.[6] We know of no other reaction mechanism with chemical precedence for the *exclusive* formation of isobutylene and hydrogen from TIBA. We cannot, however, rule out production of a small fraction of butyl radicals by homolytic bond cleavage of the surface Al–carbon bond. Such chemistry might be expected based on the methyl radical production reported for trimethylaluminum decomposition.[33] This decomposition reaction does occur, however, at much higher temperatures; the resulting aluminum films also contain carbon,[5] suggesting that radical production is but one of several higher temperature reactions that occur when β-hydrogens are unavailable.

On the basis of our thermal desorption results with isobutylene and hydrogen atoms, the rate-determining step in the mechanism of Figure 10A is (as discussed further in section 4.2) the abstraction of the β-hydrogen atom onto the aluminum surface. Such a unimolecular decomposition reaction can account for the linear dependence of the isobutylene evolution rate at 570 K on TIBA flux (Figure 2). Consistent with C–H bond breaking in this rate-determining step is the observation of a kinetic isotope effect in the decomposition of surface propyl groups as demonstrated by the data presented in Figure 6. We have also found that surface butyl groups generated from 1-iodobutane and 1-iodobutane-d_9 also show a significant isotope effect in their decomposition to evolve 1-butene and hydrogen.[25]

This rate-determining β-hydride elimination reaction is also irreversible under UHV conditions as evidenced by the lack of reaction between isobutylene and hydrogen atoms in the thermal desorption experiments (section 3.3). The lack of H,D exchange observed in our steady-state scattering experiments carried out with D_2 in the background (to test the reversibility of the surface β-hydride elimination at higher temperatures) reflects the inability of clean aluminum surfaces to readily dissociate deuterium[17,18] rather than the irreversibility of the β-hydride elimination. It has been reported that hydrogen can be dissociated in the presence of both aluminum surfaces and aluminum alkyls,[34] but we find no evidence for this synergistic formation of HD during reaction of TIBA in the presence of D_2 over Al(100) for pressures $\leq 10^{-6}$ Torr and temperatures between 370 and 550 K.

While β-hydride elimination reactions appear to dominate the chemistry of isobutyl groups on aluminum surfaces, it is instructive to consider other well-known reaction pathways for alkyl ligands in organometallic chemistry, which are apparently less facile on aluminum surfaces than β-hydride elimination. For example, it is interesting to note that, even though surface alkyl groups and H atoms are abundantly present and mobile on aluminum surfaces during CVD,[35] we observe no isobutane. This implies that β-hydride elimination is strongly favored over reductive elimination for isobutyl groups on aluminum surfaces. Reductive elimination does occur, however, on aluminum surfaces under some conditions as evidenced by the production of methane at 445 K during methanol decomposition on Al(111).[36] There is no evidence from our studies, or any others we are aware of, for the reductive coupling of alkyl groups (to evolve the dimer alkyl) on aluminum surfaces.

Another reaction pathway that we do not observe on aluminum surfaces is α-elimination from surface isobutyl groups. We specify isobutyl groups, since it has been reported by others that methyl iodide decomposes below 350 K on Al(100) to yield surface CH groups, which dehydrogenate above 400 K to give surface carbon.[37] In this latter system, α-elimination reactions seem the most logical explanation for the observed chemistry. Given this observation, it is not evident why isobutyl groups should be stable on Al(100) to temperatures >450 K. This is a notable discrepancy that other studies might reasonably address. The importance of α-elimination reactions at higher temperatures could help explain the significant carbon incorporation we observe in aluminum films grown from TIBA at $T > 600$ K, but another possible explanation is discussed below.

A particularly intriguing explanation for carbon incorporation into aluminum films grown at temperatures above 600 K is a surface β-methyl elimination reaction as shown in Figure 10B. This analogue of the β-hydride elimination reaction produces propylene (which desorbs) and surface methyl groups (the source of carbon). Unfortunately, we have been unable to discriminate the parent ions from the expected propylene desorption at high temperatures from isobutylene cracking fragments. Propylene (and methane) have been detected, however, during TIBA pyrolysis at much higher pressures.[5] There is also strong evidence for the formation of surface CH_3 groups in the high-temperature pyrolysis of TIBA from our previous studies of aluminum CVD on single-crystal silicon substrates.[7] In these studies, we found that silicon surface atoms efficiently scavenge alkyl groups and H atoms from aluminum surfaces to produce significant quantities of alkyl silanes (detected as products in the gas phase). Extensive

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(33) Squire, D. W.; Dulcey, C. S.; Lin, M. C. *J. Vac. Sci. Technol., B* **1985**, *3*, 1513.

(34) Ziegler, K.; Gellert, H.; Zosel, K.; Lehmkuhl, H.; Pfohl, W. *Angew. Chem.* **1955**, *67*, 424.

(35) The formation of diisobutylsilane when silicon atoms are present on an aluminum surface with TIBA attests to the presence and mobility of isobutyl groups and H atoms.[7]

(36) Chen, J. G.; Basu, P.; Ng, L.; Yates, J. T., Jr. *Surf. Sci.* **1988**, *194*, 397.

(37) Chen, J. G.; Beebe, T. P., Jr.; Crowell, J. E.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 1726.

mass spectroscopy studies (using specifically synthesized alkyl silanes as standards) confirmed that at least one of the silicon-containing products evolved at high temperature contains a CH_3 ligand. Our present understanding of the chemistry involved is that silicon is a passive element in this TIBA decomposition pathway; reactive fragments are generated on the predominantly aluminum surface and only subsequently diffuse and bond to silicon adatoms. By this reasoning, then, the methyl groups seen in gas-phase silanes reflect species originating in chemistry occurring *on aluminum*. The β-methyl elimination reaction implicated in the formation of this CH_3 group is not unique to aluminum surfaces. Solution β-alkyl elimination reactions have been reported for mononuclear Lu[38] and Sc[39] alkyl complexes, and it is interesting that these metals, like aluminum, formally contain one electron in their outermost atomic subshell [Al ($3p^1$), Lu ($5d^1$), and Sc ($3d^1$)]. Perhaps the best precedent for this class of reactivity, however, comes from the homogeneous chemistry of aluminum alkyls themselves.

It is well-known that a variety of aluminum alkyls will catalyze the polymerization and oligomerization of olefins.[40] In general, the growth step, that is the insertion of an olefin into an aluminum–carbon bond, is slow. High pressures of olefin are generally required to effect these reactions. The significant feature to note, however, is not the sluggish kinetics of the insertion reaction. Rather, it is the fact that the reverse process, an olefin extrusion that *involves the cleavage* of a C–C bond in the β-position, is both facile and kinetically competitive with β-hydride elimination.[41] Thus, the surface β-methyl elimination we propose appears to be well-founded. Therefore, the question arises as to why carbon deposits when methyl groups are formed on the surface. The answer here appears complex. First and foremost, the barrier to reductive elimination of alkane from surface alkyl groups and hydrogen atoms appears to be reasonably large. Second, given the facility of hydrogen desorption on aluminum, the steady-state concentration of hydrogen on this surface should be low, which would further restrict the kinetic competence of any alkane reductive elimination step. The methyl group left on the surface, therefore, presumably decomposes further by an α-hydrogen elimination process as shown in Figure 10B. As has been noted above, there seems to exist some uncertainty as to the relative energetics of this deleterious side reaction.

The fact that carbon incorporation is observed only for steady-state CVD above 600 K suggests that the activation energy for this β-methyl elimination reaction is greater than that for β-hydride elimination, which is facile at temperatures as low as 500 K. The lack of carbon incorporation in the thermal desorption experiments, in which the aluminum surfaces were heated above 700 K, is consistent with these observations and conclusions, since in the thermal desorption experiments all of the isobutyl groups are removed from the surface by β-hydride elimination below 600 K (see Figures 5, 7, and 8).

The above discussion of the chemistry of isobutyl groups on aluminum surfaces presupposes the initial adsorption of TIBA. We cannot determine from our data at what point (if any) the isobutyl ligands diffuse away from the aluminum atom to which they were initially attached. We do know that all of the isobutyl gropus behave equivalently within the resolution of our thermal desorption experiments, since only one peak is observed in TDS. We also know from our studies on the misoriented Al(111) surface (Figure 8) that the isobutyl groups must be able to diffuse on the surface, either with or without an attached aluminum atom. In as much as (1) the barriers for diffusion of surface-bound ligands are typically 20% of the heat of adsorption[42] (estimated here to be ~60 kcal/mol[43]) and (2) alkyl ligands readily exchange between terminal and bridging positions in dimeric aluminum alkyls in solution,[44] it seems probable that the TIBA ligands readily diffuse across the surface independent of the aluminum atom with which they were originally adsorbed. As discussed above, the results of experiments utilizing alkyl iodides to generate and study the chemistry of isobutyl groups on aluminum surfaces are quite supportive of these notions.[25] Comparison of these studies with those for TIBA may also help elucidate where the aluminum atom binds on the surface during the CVD process.

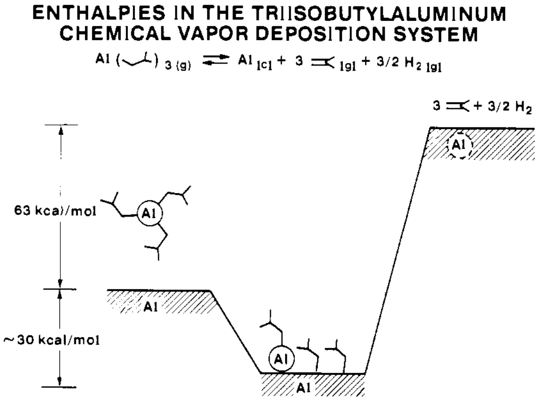
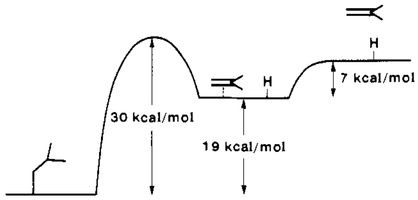


Figure 11. Approximate enthalpies under standard conditions at 298 K for the chemical vapor deposition of aluminum from triisobutylaluminum. As discussed in ref 46, the 30 kcal/mol heat of adsorption for TIBA on aluminum is probably a lower limit.


A. APPROXIMATE ENERGETICS FOR β-HYDRIDE ELIMINATION BY ISOBUTYL GROUPS BOUND TO AN ALUMINUM SURFACE

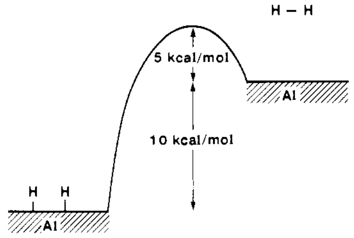

B. APPROXIMATE ENERGETICS FOR DISSOCIATIVE HYDROGEN ADSORPTION ON AN ALUMINUM SURFACE

Figure 12. Approximate energetics for β-hydride elimination from adsorbed isobutyl groups and for isobutylene and hydrogen desorption from an aluminum surface.

4.2. Thermodynamics and Surface Reaction Kinetics. As was detailed in the Results, kinetic parameters for the surface β-hydride elimination reaction were determined from thermal desorption experiments. The experimentally determined barriers to reaction [~28 kcal/mol on Al(111) and ~33 kcal/mol on Al(100)] are somewhat surprising in light of the CVD thermodynamics. As shown in Figure 11, the enthalpy change upon converting 1 mol of triisobutylaluminum into crystalline aluminum plus gas-phase isobutylene and hydrogen under standard conditions at 298 K is ~63 kcal/mol.[45] Compared to this value, the meausured barriers

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[38] Watson, P. R.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

[39] Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, 110, 976.

[40] Coates, G. E.; Wade, K. *Organometallic Compounds, Volume 1: The Main Group Elements*; Methuen: London, 1967; p 320.

[41] See: ref 5 and Eisch, J. J. Aluminum. In *Comprehensive Organometallic Chemistry*, Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. I, Chapter 6, p 610.

[42] Shustorovich, E. *Surf. Sci. Rep.* **1986**, *6*, 1.

[43] The aluminum–carbon bond energy is reported to be 61 kcal/mol: Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 2nd ed.; Harper and Row: New York, 1978; Appendix F.

[44] Reference 40, p 300.

to reaction of 28–33 kcal/mol are surprisingly small. This paradoxical situation occurs, because the enthalpy of activation measured here corresponds to converting 1 mol of isobutyl groups on the aluminum surface ($^1/_3$ mol of TIBA) into isobutylene and hydrogen. The endothermicity of 63 kcal/mol of TIBA, therefore, can be overcome by enthalpy increases of only 21 kcal/mol of isobutylene, a value well within the barrier to reaction.

This argument neglects, however, the heat of adsorption of TIBA on aluminum, which, as shown in Figure 11, is quite large (at least 30 kcal/mol of TIBA).[46] We are thus led to conclude that converting 3 mol of surface-bound isobutyl groups (1 mol of adsorbed TIBA) into isobutylene and hydrogen is actually uphill by ~93 kcal, or ~31 kcal/mol of isobutyl groups.[47] Figure 12 shows semiquantitatively how such an enthalpy change is consistent with the measured barrier to reaction. For the sake of clarity, we assume an average value of 30 kcal/mol for the barrier of the rate-limiting surface reaction. This barrier, as shown in Figure 12A, is for conversion of surface isobutyl groups to surface-bound isobutylene and H atoms. While we do not know the enthalpy change for this transformation, it cannot be greater than ~23 kcal/mol. If it were otherwise, the barrier to isobutylene desorption (~7 kcal/mol[48]) becomes greater than the barrier for the back-reaction to form isobutyl groups, and experimentally (section 3.3) we have found that heating an Al(100) surface covered with hydrogen atoms and isobutylene does not produce such species. The energetics in Figure 12A are consistent with this experimental result. The hydrogen desorption energetics in Figure 12B are also roughly consistent with experiment[49] and account for the remaining 5 kcal/mol enthalpy change per surface isobutyl group.

These thermodynamic and kinetic considerations reveal several aspects of the aluminum CVD system, which are requisite for "autocatalytic" behavior and the deposition of pure aluminum films. First and foremost, the heat of adsorption of TIBA must be greater than the barrier for β-hydride elimination (~30 kcal/mol); if this condition were not met, molecular desorption would occur preferentially and deposition would be an inefficient process. Second, this large heat of adsorption, which is almost double the heat of vaporization of TIBA (16 kcal/mol), implicates a dissociative adsorption of TIBA, with the barrier to dissociation of molecularly adsorbed species being less than ~16 kcal/mol. Third, the β-hydride elimination products (isobutylene and hydrogen) must not irreversibly adsorb on the growing aluminum surface. Finally, it also should be noted that entropy, which has not been explicitly discussed here, must play an important role in the thermodynamics of this endothermic process.

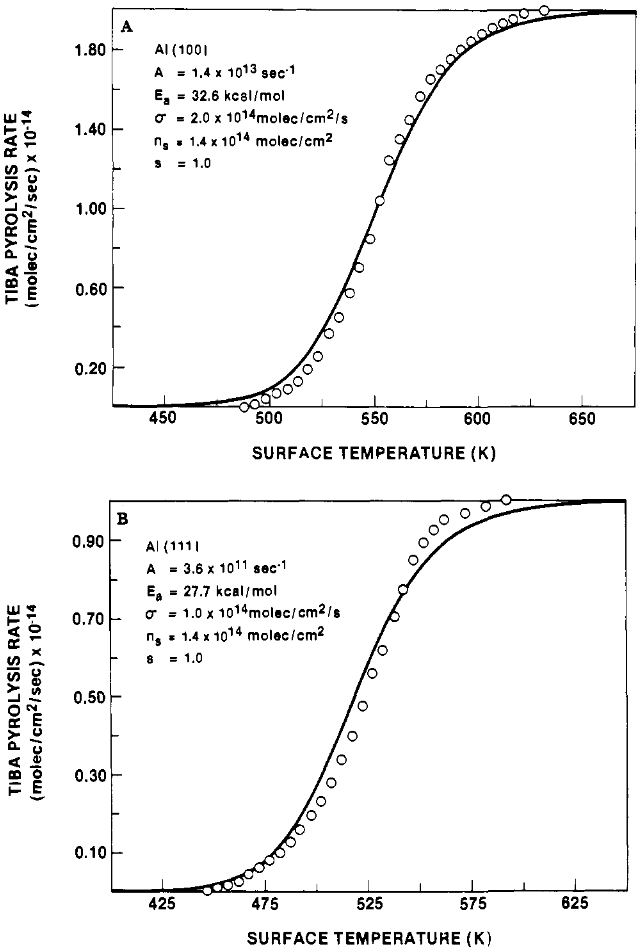

Figure 13. TIBA pyrolysis rate versus surface temperature for (A) an Al(100) substrate and (B) an Al(111) substrate. The points are the experimental values, and the curves are model fits based on the parameters listed and discussed in the text.

4.3. Prediction of Aluminum Deposition Rates.[50] Since we find that adsorbed TIBA decomposes on aluminum surfaces to deposit metal cleanly at typical CVD temperatures, it seems probable that the steady-state aluminum deposition rate is determined by the rate of this surface reaction. To test this hypothesis, we have developed a model that utilizes the kinetic parameters for the surface reaction determined by thermal desorption to predict steady-state aluminum deposition rates such as those shown in Figures 1 and 2. In this model, we assume the following: (1) the rate of deposition is limited (for infinite flux) by the rate of the surface reaction; (2) the kinetic parameters for the surface reaction are independent of surface coverage; (3) TIBA molecules incident on empty sites have a sticking probability, *s*. The rate of adsorption and the rate of the surface reaction are thus given by

$$\text{rate of adsorption} = \sigma(1 - \theta_T)s \qquad (1)$$

$$\text{rate of isobutylene production} = A3\theta_T n_s \exp[-E_a/RT] \qquad (2)$$

where σ = TIBA flux, θ_T = fractional surface coverage of TIBA, s = sticking probability, A = Arrhenius preexponential factor, E_a = activation energy, R = gas constant, T = temperature, and n_s = number of adsorbed TIBA per unit area at saturation coverage. At steady state, the rate of TIBA adsorption must be $^1/_3$ the rate of the production of isobutylene given the assumptions above,[51] allowing us to solve for θ_T:

$$\theta_T = \left[\frac{An_s}{\sigma s} \exp[-E_a/RT] + 1 \right]^{-1} \qquad (3)$$

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(45) This value was calculated with heats of formation given by Egger in ref 6. Tabulated values of C_p for H_2, Al, and isobutylene and an estimation for TIBA at 400 K suggest that the enthalpy change for this reaction at the actual deposition temperature of 550 K is lower by ~10 kcal/mol.

(46) This estimation is based on two observations: (1) molecular desorption of TIBA from aluminum surfaces is not observed even at saturation coverage, suggesting that the barrier to molecular desorption must be at least comparable to that for β-hydride elimination (which is ~30 kcal/mol); (2) if TIBA adsorption occurs as shown in Figure 11 where the ligands diffuse across the surface, then the heat of adsorption of TIBA should be of the order of the heat of adsorption of an aluminum atom. Given that the heat of vaporization of aluminum is 68 kcal/mol, the heat of adsorption of TIBA may in fact be substantially greater than 30 kcal/mol.

(47) Even though the adsorbed isobutyl groups in Figure 11 are shown as inequivalent, our thermal desorption experiments show that all of the isobutyl groups have equivalent decomposition rates. Surface diffusion is therefore implicit in the schematic representation in Figure 11.

(48) This barrier is calculated from thermal desorption spectra of isobutylene adsorption on Al(100) utilizing the desorption maximum of 130 K and the analysis of Redhead.[28] A preexponential factor of 10^{13} s^{-1} is assumed.

(49) On the basis of the desorption peak temperature of 330 K and the narrow peak width [~30 K fwhm], we estimate that the barrier to hydrogen desorption is at least 15 kcal/mol.[17] A barrier to adsorption of at least 5 kcal/mol is necessary to account for the observed sticking probability of less than 0.001 for room-temperature H_2 on Al(100).[18]

(50) A more detailed account of the model presented here has been given: Bent, B. E.; Dubois, L. H.; Nuzzo, R. G. *Mater. Res. Soc. Symp. Proc.*, in press.

(51) The rate of the surface reaction is per each isobutyl group. Since TIBA has three isobutyl groups, the steady-state rate of adsorption (rate of aluminum deposition) is $^1/_3$ the rate of the surface reaction.

Substituting for θ_T in eq 2, and noting that the rate of aluminum deposition is $^1/_3$ the rate of olefin formation, gives the rate of deposition as a function of parameters we presumably know:

$$\text{rate of aluminum deposition} = \frac{An_s \exp[-E_a/RT]}{\frac{An_s}{\sigma S}\exp[-E_a/RT] + 1} \qquad (4)$$

Using the kinetic parameters determined from the thermal desorption experiments on Al(111) and Al(100) surfaces, assuming a sticking probability of 1, and taking $n_s = 1.4 \times 10^{14}$ TIBA/cm^2,[52] we obtain the fits to the experimental data points as shown in Figure 13. The only parameter adjusted in this figure was the incident flux of TIBA. This parameter could not be accurately measured for several reasons. First, a TIBA/isobutylene mixture of unknown composition enters the chamber. Second, the crystal was positioned directly in front of the mass spectrometer skimmer rather than facing the doser for these experiments (we wished to image only the sample). It is noteworthy, however, that the fluxes used in the fits of Figure 13 are within a factor of 2 of estimates based on the chamber background pressure of about 1×10^{-6} Torr during these experiments. The remarkable agreement between the experimental results and the model strongly substantiates the hypothesis that surface reactions control the rate of steady-state aluminum deposition from TIBA. The systematic discrepancy between experiment and model at high temperatures for both surfaces probably reflects a depletion in the TIBA flux to the surface.

It should be noted that the excellent agreement between model and experiment in Figure 12 does not necessarily imply that the kinetic parameters determined from the thermal desorption experiments are extremely accurate. There can be compensating effects between pairs of parameters in the model (for example, between the preexponential factor and the number of surface sites) that will offset individual inaccuracies. We believe, however, that the activation energies are accurate to better than 2 kcal/mol and the preexponential factors to within $^1/_2$ an order of magnitude. The kinetic parameters for β-hydride elimination on Al(111) are nearly identical with those reported for gas-phase β-hydride elimination of one isobutyl group from TIBA ($E_a = 26.6$ kcal/mol and $A = 1.6 \times 10^{11}$ s^{-1}).[6] This result suggests that the β-hydride elimination on Al(111) may occur at individual aluminum atoms. It is not obvious, however, why the kinetic parameters and the β-hydride elimination rate are so different for TIBA on Al(100), and this point is under investigation.[53]

Assuming that surface reactions also control the steady-state deposition of aluminum in CVD reactors (which typically operate using a TIBA pressure of ~1 Torr), we should be able to predict the aluminum deposition rates using our model. Our rate predictions are shown in Figure 14 and compared with the aluminum deposition rates reported by Cooke et al.[3] The agreement between our predictions derived from monolayer thermal desorption experiments in ultrahigh vacuum and the experimental results at orders of magnitude higher pressure is quite remarkable. Since perfect single-crystal aluminum growth was assumed in the predicted growth rates, part of the discrepancy in Figure 14 could be due to the higher real surface areas, which characterize rough CVD aluminum films on SiO$_2$. We also note that, while the net macroscopic growth rate is actually an average of the different growth rates for different crystal faces, it is probable that the CVD film is strongly (111) textured,[4] consistent with the measured growth rate being closest to the predictions for Al(111).

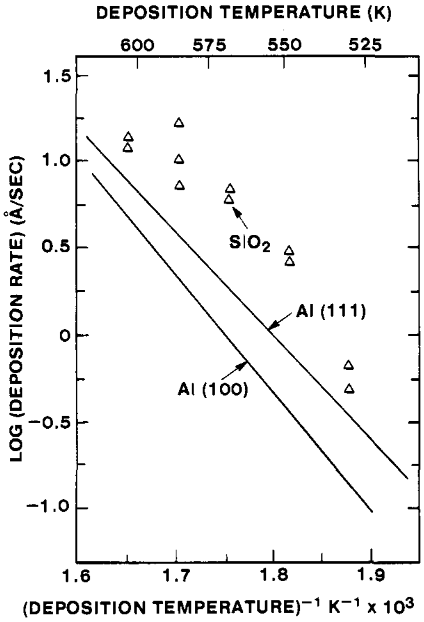

Figure 14. Predicted aluminum deposition rates from TIBA on Al(111) and Al(100) substrates (solid lines) and measured deposition rates on SiO$_2$ (points) as a function of substrate temperature. The experimental values are from ref 3. The predictions are based on the model for aluminum deposition from TIBA discussed in the text. The necessary kinetic parameters for the model were determined from monolayer thermal desorption experiments, and an infinite flux of TIBA was assumed in predicting the deposition rates.

5. Conclusions

Our results show that aluminum surfaces readily effect the decomposition of TIBA at surface temperatures above 500 K to deposit aluminum and evolve isobutylene and hydrogen. Below 600 K, the deposited aluminum is carbon-free, but at higher temperatures carbon incorporation is observed. At all surface temperatures between 500 and 700 K the aluminum growth is crystalline, and the growing film adopts the orientation of the (111) or (100) substrate used in these studies. The surface reaction, which is responsible for carbon-free deposition below 600 K and which also determines the rate of aluminum deposition, is β-hydride elimination. This reaction is 2–5 times faster on Al(111) than on Al(100) in the temperature range of 570–470 K. Our studies suggest that the surface reaction responsible for carbon contamination above 600 K is a β-methyl elimination. The overall thermodynamics for deposition of carbon-free aluminum from TIBA is endothermic by about 60 kcal/mol of TIBA; the measured barrier to reaction is 28 [Al(111)] or 33 [Al(100)]] kcal/mol of adsorbed isobutyl groups. We have utilized these kinetic parameters determined from monolayer thermal desorption experiments along with a simple model to predict the rate of steady-state aluminum deposition from TIBA at pressures ranging from 10^{-6} to 1 Torr.

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(52) This value was approximated from the exposure necessary to achieve saturation coverage in the TIBA thermal desorption experiments. It is roughly consistent with the van der Waals radii of TIBA.

(53) It is interesting that the difference between the Al(111) and Al(100) work functions [4.24 vs 4.41 eV: Grepstad, J. K.; Gartland, P. O.; Slagsvold, B. J. *Surf. Sci.* **1976**, *57*, 348] is ~5 kcal/mol, the difference between the barriers for β-hydride elimination from isobotyl groups on these surfaces!