Quantitative Infrared Spectroscopy of Tetrakis(dimethylamido)Titanium for Process Measurements

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In situ infrared (IR) spectroscopy has proven to be an extremely valuable tool for understanding various aspects of chemical vapor deposition (CVD) and atomic layer deposition (ALD). Solid film deposits, gaseous precursors and by-products, and growth surfaces are all of interest in these processes, and IR spectroscopy is capable of providing useful data for each. Qualitative measurements are sometimes sufficient, but quantitative spectroscopy is often desired for work involving process monitoring or process development. Relating absorbance to concentrations can be problematic for surfaces and solid deposits due to interactions, dielectric screening, etc., but measurements of the gas phase are straightforward if absorptivities are known.

Efforts to obtain accurate IR reference spectra of CVD and ALD precursors, however, have been limited.1 Commercial quantitative spectral libraries, if they include any precursors at all, typically contain only the most common ones (e.g., SiH4 and WF6). This is despite the use of IR spectroscopy for process monitoring in manufacturing2 and for process development in the laboratory.3,4 There is a need, therefore, for carefully obtained spectra of the less common precursors and for a general method of obtaining them.

This work presents a static measurement for determining the IR absorptivities of low vapor pressure organometallic compounds used as precursors for CVD and ALD. We use Fourier transform IR (FT-IR) spectroscopy to this end. Since the focus of this work is related to CVD and ALD processes where the compounds are typically heated to increase their vapor pressure, we obtain reference spectra at elevated temperatures. Heated samples are known to cause photometric errors in FT-IR spectroscopy, so we use a setup that is demonstrated to provide correct spectra. The apparatus and method for emission correction are discussed fully in the Experimental section.

Quantitatively accurate IR spectra of tetrakis(dimethylamido) titanium (TDMAT), Ti[N(CH3)2]4, are measured in the temperature range of (352 to 476) K. TDMAT is an alkylamido organometallic compound, a class of molecules that has found widespread use as CVD and ALD precursors in the semiconductor industry. TDMAT, in particular, is commonly used for the CVD of TiN and is under investigation for the ALD of TiO2. Qualitative IR spectra of TDMAT have been reported a number of times in the literature,5–11 which offers an opportunity to compare the results to previous studies and to elucidate the discrepancies. The temperature-dependent IR absorptivity is presented in the Results section, and a comparison to prior results can be found in the Discussion section. We believe the observed trends may be of interest to those engaged in modeling reactions involving organometallic precursors.12

While potentially useful for understanding molecular structure and reactivity, our motivation for obtaining the reference spectra is process monitoring, and we analyze our findings within that context. We discuss the implications of the temperature-dependence of the absorptivity for process measurements based on FT-IR spectroscopy. Using the data obtained in this paper, results potentially could be analyzed to yield both the gas temperature and the molar density. Additionally, we discuss implications for other IR-based methods under development.

In preparing spectra at the upper temperature limit of our present setup (476 K), we had expected to observe the products of thermal decomposition, which have been directly observed in previous studies.7,10,11,13 Many phenomena in thin film deposition have been attributed to thermal decomposition,14–18 so measuring the products could provide important, practical insights. We find, however, that TDMAT is much more stable at 476 K than the literature indicates. In fact, we observe that decomposition at this temperature is possibly 105 times slower than previously reported.11 Thus, our findings also have very practical implications for precursor screening.

Experimental

Methods and analysis.— A model RS-10000 FT-IR spectrometer (Mattson Instruments, Madison, WI) is used to measure samples in a custom-built gas cell. The spectroscopic parameters used in this study are listed in Table I. The interferometer has mirrors consisting of corner-cube retroreflectors, a KBr beamsplitter is used, and the collimated beam is incident at a 45° angle. The Jacquinot stop (J-stop) is a motorized iris. Unfortunately, the size of the aperture is not known from the instrument software or its documentation, but “5%” is specified in the software which corresponds to a J-stop diameter of roughly 2 mm. The interferometer, the detector compartment, and the small volume between the cell and sample compartment wall are purged with the boil-off gas from a liquid nitrogen dewar. The beampath between the gas cell and the sample compartment walls is sealed using closed-cell silicone foam. As will be discussed in the next section, half of the collimated beam leaving the interferometer is blocked.

We use a cryogenic mercury cadmium telluride (MCT) detector for these measurements. The useful wavenumber range of the detector is (420 to 4800) cm⁻¹, but the ZnSe windows used for the gas cell limit us to (v < 550) cm⁻¹. A linearizing pre-amplifier is manually adjusted to compensate for the detector non-linearity. Using the transformed single-beam spectra, we characterize the linearity through the ratio of the intensity below the detector low-wavenumber cutoff to the maximum intensity; ratios of <0.1% are thus obtained.

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1Certain commercial equipment, instruments, and materials are identified in this publication to adequately specify the experimental procedure. Such identification in no way implies approval, recommendation, or endorsement by NIST, nor does it imply that the equipment, instruments, or materials identified are necessarily the best available for the purpose.
Furthermore, we restrict our conditions to those where the maximum absorbance is below 0.2 absorption units (AU).

Background and sample single-beam spectra are obtained from averaging 512 and 128 individual interferograms, respectively, which respectively require 9.4 min and 2.3 min. The background scans are initiated after the cell has been evacuated below 0.13 Pa for 60 s. After a set of background scans are complete, the sample is introduced into the cell for a set amount of time, and a sample spectrum is obtained. The cell is then purged with purified helium and subsequently evacuated. Absorbance spectra \( A(\tilde{\nu}) \) are calculated from the base-10 logarithm of the transmittance \( T(\tilde{\nu}) \). With the cell in place, the root-mean-square (rms) noise is 0.03% T between 2000 cm\(^{-1}\) and 2200 cm\(^{-1}\). Baseline correction of the absorbance spectra is made by subtracting a cubic function obtained through fitting of points outside the absorbing regions.

The cell and connected tubing are constructed of electropolished stainless steel, and all joints except at the windows are either welded or sealed using stainless steel gaskets. The gas cell is a single-pass design with a measured length of 12.704 \( \pm \) 0.005 cm; its inner and outer diameters are 25 mm and 76 mm, respectively. The two windows are sealed with fluororubber o-rings in a differentially pumped configuration, which required use of 50-mm diameter windows to accommodate the two concentric o-rings. The windows are ZnSe and wedged to reduce fringes in the spectra and back reflections to the interferometer. Pneumatic-driven diaphragm valves admit the dry forepump. The purified He purge gas is admitted through a 50 L/s turbomolecular/molecular drag hybrid pump backed with a 250 L/s cryogenic liquid nitrogen cold finger. When the pulsed pressure reaches a constant value, DMA is aspirated into the cell for a set amount of time, and a sample spectrum is obtained. The value of \( n \) is calculated using Eq. 3. The uncertainty in the \( n \) product is estimated to be \( \pm 1\% \) and is dominated by the error in \( T_p \). The measurement uncertainty in \( A(\tilde{\nu}) \) potentially comes from non-linearity in the MCT detector, residual baseline instability, and noise. An unweighted least-squares fit of \( A(\tilde{\nu}) \) to \( n \) is made for each value of \( \tilde{\nu} \). Calculated uncertainties in the slope \( A(\tilde{\nu}) \) include direct contributions from the error in \( A(\tilde{\nu}) \) and indirect contributions from that of \( n \) and \( l \). The \( y \)-intercepts were also obtained from the fits although they should ideally be zero. The implications of the \( y \)-intercept are discussed further in the Results section.

Sample emission correction.— IR emission by a heated sample and cell is known to cause systematic errors in FT-IR spectroscopy because it can enter the interferometer and return modulated to the detector. The magnitude of the error depends on the optics, the temperatures of components, and the spectral range, so no universal correction can be applied across spectrometer designs. One solution is to measure interferograms with the source on and off. Additionally, the use of corner-cube or cat’s eye retroreflectors in the interferometer has been reported to decrease the effect of emission by spatially offsetting the optical paths taken by radiation emitted by the sample/cell versus that from the IR source. In most interferometers that incorporate retroreflectors, however, their purpose is to reduce the effects of mirror tilt, and the beam from the IR source is centered within the corners of the mirror cubes. In such cases, there is no built-in offset between the emitted radiation from the cell and that from the IR source. That is the case with the spectrometer used in this study.
To obtain a physical offset from the retroreflectors, a half-beam block is used. This was implemented using an internal mirror that slides into the collimated beam leaving the interferometer. The intended purpose of the mirror is to send the beam outside the spectrometer housing to an external apparatus, but by repositioning the mirror half-way into the beam, half of the radiation from the IR source reaches the detector while modulated radiation from the gas cell is directed outside. By comparing spectra corrected for emissivity to uncorrected spectra, we find that sample emission at 476 K causes an apparent 18% increase in some low-\( \tilde{\nu} \) peaks. Comparing the effectiveness of our half-beam setup to the source-on/source-off method, we find they agree to within 2%. Part of the disagreement between the two correction methods is likely due to the slow loss of TDMA T using the source-on/source-off method. During that procedure, the charge of TDMA T must remain in the cell while the source cools for 3 minutes during which time the TDMA T absorbance (using the half-beam block method) is observed to drop slightly. Because of this, we consider results from the half-beam block method to be more accurate. The drop in absorbance is discussed in terms of decomposition within the Discussion section.

Results

The emissivity-corrected \( \alpha(\tilde{\nu}) \) of TDMA T at 352 K is displayed in Fig. 1 along with that of DMA. Similar to all previously published spectra of TDMA,\cite{7-11} it displays intense peaks at around 592 cm\(^{-1}\) and 946 cm\(^{-1}\) and in the C–H stretch region (2700 cm\(^{-1}\) to 3000 cm\(^{-1}\)). In the C–H stretch region, an intense, low-frequency Bohlmann band at 2777 cm\(^{-1}\) is apparent. This feature is due to the nitrogen lone pair interacting with a trans diaxial C–H bond.\cite{12} Also in agreement with prior results, the TDMA T spectrum is distinct from DMA, which lacks the above features.\cite{23}

Detailed portions of the \( \alpha(\tilde{\nu}) \) of TDMA are presented in Fig. 2 as a function of \( T_g \), and these data are provided online in tabulated form.\cite{24} Uncertainties vary from \( \pm 0.6 \text{ m}^2/\text{mol} \) at 550 cm\(^{-1}\) to \( \pm 0.1 \text{ m}^2/\text{mol} \) through most of the \( \alpha(\tilde{\nu}) \) spectrum above 1000 cm\(^{-1}\). The fitted y-intercepts are negative for \( \tilde{\nu} \) values where strong absorption appears: Values are around \( -2 \times 10^{-3} \text{ AU} \) near 946 cm\(^{-1}\) and in the C–H stretch region. We believe this deviation is due to a small amount (approximately 0.5 Pa) of DMA that is formed in the cell. While easily observable with a capacitance manometer, at such low pressures, DMA would not be detected spectroscopically under the current conditions. The \( \alpha(\tilde{\nu}) \) of DMA is over an order of magnitude lower than that of TDMA T (see Fig. 1). Given the low calculated uncertainty in \( \alpha(\tilde{\nu}) \) for TDMA, the DMA partial pressure is generated reproducibly with each TDMA T injection. If the He used for purging the cell contains a minute amount of H\(_2\)O, it would easily explain this.

Figure 1. Molar absorptivity spectra of vapor-phase TDMA T (black curve, left axis) and DMA (red curve, right axis) obtained at 352 K. Note that the absorptivity of TDMA T is over an order of magnitude greater than that of DMA.

Figure 2. The molar absorptivity of TDMA vapor as a function of temperature in the vicinity of (a) the Ti–N stretch at 592 cm\(^{-1}\); (b) the C\(_2\)N symmetric stretch at 946 cm\(^{-1}\); (c) C\(_2\)N asymmetric stretch at 1057 cm\(^{-1}\) and CH\(_3\) rock modes at 1127 cm\(^{-1}\) (shoulder), 1152 cm\(^{-1}\), and 1250 cm\(^{-1}\); (d) the symmetric and asymmetric CH\(_3\) deformations at 1424 cm\(^{-1}\) and 1457 cm\(^{-1}\), respectively; and (e) the C–H stretch bands at 2777 cm\(^{-1}\) (Bohlmann band), 2824 cm\(^{-1}\), 2851 cm\(^{-1}\) (shoulder), 2864 cm\(^{-1}\), 2916 cm\(^{-1}\), 2942 cm\(^{-1}\), and 2961 cm\(^{-1}\) (Ref. 7).
It is apparent from Fig. 2 that the peaks decrease in strength and broaden with increasing $T_g$ in a complicated manner. In particular, the intensity of the Bohlmann band (Fig. 2e) decreases by 35%, as the temperature increases from 352 K to 476 K while other C–H stretch modes change much less. The peak near 946 cm$^{-1}$ broadens dramatically with increasing temperature (Fig. 2b), but the decrease in the Bohlmann band is accompanied by very little broadening (Fig. 2e). Furthermore, several peaks in the fingerprint region below 1500 cm$^{-1}$ are observed to redshift with increasing temperature: 946 cm$^{-1}$ (Fig. 2b), 1152 cm$^{-1}$ (Fig. 2c), and 1250 cm$^{-1}$ (Fig. 2c). Others remain stationary: the peak at 592 cm$^{-1}$ (Fig. 2a), the shoulder at 1127 cm$^{-1}$ (Fig. 2c), and the peaks in the C–H stretch region (Fig. 2e). Two other peaks appear to blueshift as the temperature increases from 352 K to 476 K: the Bohlmann band (2777 cm$^{-1}$) by about 0.8 cm$^{-1}$ and the peak near 1152 cm$^{-1}$ by about 0.3 cm$^{-1}$. These slight changes may be due to broadening of neighboring peaks, however, and are not necessarily due to changes in the vibrational modes.

While the molecular origins of these phenomena are beyond the scope of this paper, we note that they are systematic. The redshifting of the peaks near 946 cm$^{-1}$, 1152 cm$^{-1}$, and 1250 cm$^{-1}$ is plotted in Fig. 3. The positions are obtained by fitting each to a peak function on a linear background using the Levenberg-Marquardt method. The peaks near 946 cm$^{-1}$ and 1250 cm$^{-2}$ are fit to Voigt bandshapes while the peak near 1152 cm$^{-1}$ is obtained by simultaneously fitting it and the shoulder at 1127 cm$^{-1}$ to Gaussians. In each case, the position is found to linearly decrease with increasing temperature; the 946 cm$^{-1}$ peak center is notable more sensitive to temperature than the others. The fitted parameters from the linear fits are presented in Table II.

Temperature has a significant effect on peak positions and broadening, but it does not affect the integrated intensities. Within the seven regions listed in Table III, we find no statistically significant variation in the integral of $\alpha(\nu)$ as $T_g$ changes. This validates the method used for emissivity correction since sample emission would increase the apparent intensities of low-$\nu$ bands with increasing temperature (see the preceding section). We therefore average the integrated values across temperatures and present the results in Table III.

### Discussion

**Comparison to previous results.**— Previous IR measurements of TDMAT have presented contradictory peak positions. We believe the discrepancies can be largely explained by the temperature-dependences observed in this paper. In Fig. 3, we have plotted literature values for the peaks in question. With the exception of the two early papers that used dispersive IR spectroscopy to examine TDMAT samples in solution (represented as triangles), there is generally good agreement with the temperature trends of our data. Differences in spectral resolution could explain some of the disagreement. Additionally, the reported precision of all previous reports is 1 cm$^{-1}$, so numerical rounding is another factor. (The excellent agreement between our data and that of Ref. 8 is likely because of their selection of 363 K, which coincidentally results in peak locations very close to whole number values.)

The focus of previous work was primarily on the reporting of peak locations, so only semi-quantitative comparisons of peak shape and intensities are possible. The effect of sample emission at high temperature was neglected, and very high absorbance values were often measured with non-linear MCT detectors. With the exception of Ref. 8, only low resolution spectra have been reported, which introduces another complication. With those caveats in mind, we note that the spectra of Refs. 8 and 11 are similar to what we measure at comparable temperatures. Spectra obtained at 332 K and 445 K in Ref. 7 shows a decrease of the 2777 cm$^{-1}$ peak with increasing temperature as we observe (Fig. 2e). However, the degree to which it is has decreased with respect to the other C–H stretch modes at 445 K is far beyond what we find at 476 K. This suggests the TDMAT vapor was hotter in that study than reported, but contributions from other species with C–H bonds may also be a factor. A similar inconsistency

<p>| Table II. Parameters describing the linear temperature-dependence of peak position (Fig. 3). |
|---------------------------------|---------------------------------|---------------------------------|
| Approximate peak Extrapolated peak Slope |</p>
<table>
<thead>
<tr>
<th>center (cm$^{-1}$)</th>
<th>center at 0 K (cm$^{-1}$)</th>
<th>($\times 10^{-2}$ cm$^{-1}$/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>946</td>
<td>962.8 ± 0.2</td>
<td>−4.05 ± 0.06</td>
</tr>
<tr>
<td>1152</td>
<td>1162.2 ± 0.1</td>
<td>−2.29 ± 0.03</td>
</tr>
<tr>
<td>1250</td>
<td>1202.0 ± 0.2</td>
<td>−2.81 ± 0.04</td>
</tr>
</tbody>
</table>

| Table III. Integrated absorptivity bands (Fig. 2). They are found to be insensitive to temperature and are averaged across temperatures. |
|-----------------|-----------------|-----------------|
| Spectral region Integrated absorptivity |
| (cm$^{-1}$) | (× 10$^{-3}$ m/mol) |
|-----------------|-----------------|-----------------|
| 550–630 | 9.4 ± 0.3 |
| 900–1000 | 24.9 ± 0.1 |
| 1025–1090 | 1.7 ± 0.1 |
| 1100–1200 | 6.2 ± 0.4 |
| 1200–1300 | 7.4 ± 0.2 |
| 1400–1510 | 4.46 ± 0.08 |
| 2635–3000 | 67.3 ± 0.3 |

![Figure 3](https://example.com/image.png)

Figure 3. The temperature dependence of peak positions. Linear fits to the data are solid lines, and the dashed lines are extrapolations. Reported literature values are indicated on the same plot; the error bars, in this case, are intended to indicate their reported precision (1 cm$^{-1}$) and do not denote statistical uncertainty. (Note that the actual experimental uncertainty in the data from Refs. 5 and 6 is expected to be much greater than the precision because of the use of dispersive IR spectroscopy.)
is found in Ref. 10 where spectra obtained from TDMAT flowing through a cell at 600 K exhibit peaks at 2777 cm\(^{-1}\) that are greater than the other C–H stretch modes. This indicates the gas was cooler than the cell.

**Implications for process monitoring.**—The quantitative FT-IR spectroscopy of gas-phase TDMAT (and likely other organometallics) may be complicated by the changes in \(\alpha(n)\) with \(T_g\) (Fig. 2). Previously, we used classical least-squares analysis to determine \(n\) of another alkylamido precursor, tetrakis(ethylmethyleneimido)dihafnium (TEMAH), \(\text{Hf[N(CH}_2\text{CH}_3\text{)(CH}_3\text{)}_2]\_4\), in an ALD reactor.\(^{25}\) In that study, the reference spectrum was obtained at a temperature similar to that of the reactor, so no significant error is expected. In general, direct application of least-squares regression analysis to in situ spectra requires \(T_g\) of the process to be known so that the correct \(\alpha(n)\) can be measured at the same \(T_g\). If \(T_g\) in the process is to vary, then \(\alpha(n)\) must be measured over the temperature range of interest as we do here. However, once \(\alpha(n)\) is determined over a range of \(T_g\), new capabilities become available. For example, an algorithm that first determines \(T_g\) using the position of the 946 cm\(^{-1}\) peak (Fig. 3 and Table II) and then uses an interpolated \(\alpha(n)\) spectrum could, in principle, provide both \(n\) and \(T_g\) of TDMAT. Alternatively, a non-linear fit to simultaneously obtain \(n\) and \(T_g\) may also be possible. These data could be extremely useful for verifying models of heat and mass transport in process environments.

The present study has found that the integrated band intensities are not affected by \(T_g\). Integrated band intensities may be the preferable method for obtaining \(n\) from in situ FT-IR spectroscopy if there is no overlap between the absorption bands of the gas-phase components and if sample emission can be eliminated. For TDMAT, the (550 to 630) cm\(^{-1}\), (900 to 1000) cm\(^{-1}\), and (1200 to 1300) cm\(^{-1}\) ranges show minimal overlap with DMA absorption features (see Fig. 1 noting the differing vertical scales.) The advantages of this approach are that \(T_g\) of the process need not be known and that less effort can be spent on obtaining reference spectra.

This work can be extended to other IR-based measurements besides FT-IR spectroscopy. Filter IR photometers are relatively simple devices that monitor intensity within the spectral band of a bandpass filter. While offering no spectroscopic information within the bandpass, they can provide good time resolution and sensitivity.\(^{2,26,27}\) Furthermore, if the IR source is amplitude modulated, sample emission does not affect the measurement. Unfortunately, a Beer’s law relationship between \(n\) and the measured signal is not necessarily expected from a filter photometer, so calibration is typically necessary. Furthermore, variability between IR filters requires each to be calibrated individually. The data in Fig. 2 could be used to calculate the calibration curve of a filter photometer system if the \(\alpha\)-dependence of the IR source, filter transmission, and detector response were known. If the bandpass is narrow, knowing only the transmission of an individual filter may be adequate. Therefore, variability in IR filters need not necessitate calibrating each one individually if \(\alpha(n)\) is known.

We have previously utilized an external-cavity quantum cascade laser (EC-QCL) with a tuning range between about 925 cm\(^{-1}\) and 995 cm\(^{-1}\) as a process diagnostic during ALD.\(^{28}\) The system was used to monitor TEMAH, which has an intense peak at 979 cm\(^{-1}\) analogous to the 949 cm\(^{-1}\) peak from TDMAT. The beam reaching the detector was both modulated and high intensity, so complications from sample emission are not expected. However, the temperature dependence we have found for TDMAT (Fig. 2b) is also likely exhibited by TEMAH. This presents a difficulty for utilizing laser-based measurements for determining \(n\) since \(T_g\) must also be known to use the correct \(\alpha\). However, with the broad tuning capabilities of an EC-QCL, one could possibly implement an algorithm that first determines \(T_g\) from peak position as discussed above.

**Decomposition.**—Past investigations of TDMAT interacting with heated surfaces have frequently found that decomposition occurs at modest temperatures. To investigate the degree to which decomposition may influence our measurements, we examine a sample of TDMAT held at 476 K for 30 min. After being admitted at a pressure of 29 Pa, the cell pressure is observed to rise linearly at a rate comparable to the leak rate of the cell with no sample present. Over the course of the experiment, the absorbance of the peak near 946 cm\(^{-1}\) decreases by 13% (i.e., 3.8 Pa) while the only new feature is a weak (\(7 \times 10^{-4}\) AU), broad band around 730 cm\(^{-1}\). This band is likely the N–H bend mode of DMA,\(^{23}\) which absorbs with \(\alpha \approx 5 \text{ m}^2/\text{mol}\) (Fig. 1). The calculated partial pressure of DMA after 30 min is 4 Pa, which is what one would expect if the consumed TDMAT is converted to DMA with a 1:1 stoichiometric ratio. The nearly linear decrease in TDMAT absorbance indicates zero-order kinetics. However, if pseudo first-order kinetics is assumed, a rate constant of (6.4 \(\pm 0.7\)) \(\times 10^{-4}\) s\(^{-1}\) is obtained. This is over two orders of magnitude below what has previously been reported at this temperature.\(^{11}\) However, because of the larger area of the heated surfaces and smaller volume of our gas cell, we estimate that surface reactions (if responsible for the observed decrease in TDMAT molar density) are actually 10\(^3\) times slower. The systematic error in our high-temperature spectra due to decreasing TDMAT molar density is therefore very small for our 2 minute acquisition times (\(<1\%)\).

We cannot definitely say whether the lost TDMAT in our experiment is due to thermal decomposition or to reaction with atmospheric gases (i.e., \(\text{H}_2\text{O}\)) slowly leaking into the cell. Regardless of the cause, the conversion of TDMAT to DMA is extremely slow. The lack of rapid thermal decomposition is remarkable because it has been observed so frequently in previous studies of TDMAT. In Ref. 11, FT-IR spectroscopy monitored the gas phase while TDMAT was exposed to a heated surface; DMA was found to be the majority product, which is in agreement with our observations, but the minor products methane and methylmethyleneimine (MMI), \(\text{H}_2\text{C} = \text{NCH}_2\text{CH}_3\), are absent from our spectra. Possibly, the same decomposition reactions are occurring in both experiments, but the slower rate observed in our work produces the minor products at concentrations below our detection limit. Studies using mass spectrometry, however, have found that DMA, methane, and hydrogen were evolved from metal surfaces that were doped with TDMAT and annealed, but no evidence for MMI was found.\(^{29}\) The decomposition reaction observed using FT-IR spectroscopy in Ref. 7 is apparently very different from what others have observed. New bands around 535 cm\(^{-1}\), 660 cm\(^{-1}\), and 780 cm\(^{-1}\) appeared in the gas-phase spectrum when the sample was introduced at 445 K. These cannot be assigned to DMA, MMI, or methane. We also note that gas chromatography (GC) has been used to identify products from TDMAT decomposition in the GC column.\(^{13}\) At 425 K, DMA was observed as well as tetramethylhydrazine, \(\text{N}_2\text{N}_2\text{N}_2\text{-tetramethylmethanediamine},\) and \(\text{N}_2\text{N}_2\text{N}_2\text{-trimethylmethanediamine.}\) Besides DMA, there is little agreement between studies on the gas-phase products of TDMAT decomposition.

Given the simplicity of our experimental setup and lack of evidence for rapid decomposition, it appears that the results from other studies involving modest heating (i.e., 425 K to 475 K) were not due to the intrinsic instability of TDMAT. Instead, it seems more likely that reactive surfaces are necessary for appreciable thermal decomposition to occur at those temperatures. Previously, mass spectrometry-based flow tube studies found TDMAT decomposed primarily on surfaces below about 480 K with gas-phase reactions becoming significant above that; unfortunately, the nature of the surfaces was not examined.\(^{30}\) Driessen et al., examining a heated Ti carbonitride surface, proposed a low-temperature mechanism in which surface-bound hydrogen and hydrogen-containing moieties were responsible for TDMAT decomposition.\(^{11}\) This model would explain the slow decomposition here if the surfaces in our gas cell are sufficiently poor at providing hydrogen to react with adsorbed TDMAT. The origin of the bands observed in Ref. 7 remains unclear based on our experiments, but errors in the temperature measurement (as noted in the Comparison to Previous Results above) may explain it. Contact with unintentional heated metal surfaces that oxidized stainless steel is another plausible explanation. It is known that the surface reactions of TDMAT proceed very differently depending on the nature of the surface.\(^{2,29}\) This may further explain differences between these studies and the GC results.\(^{13}\)
since the stationary phase of the GC column would be expected to exhibit surface chemistry that is very different from any other surface investigated.

The fact that we cannot duplicate the rates or products of TDMA decomposition reported in the literature indicates that prior results are specific to the experimental setups employed. The fact that the reaction products differ between studies (see above) supports this statement. Thus, vapors of TDMA (and other alkylamido organometallics) may be more stable under certain conditions than is often inferred.14–16 Our findings, in the context of other studies, suggest that the decomposition rate depends critically on the surfaces in which the vapor is in contact. The use of TDMA for the ALD of next-generation high-k dielectrics like titanates, which require high processing temperatures, should not be discounted without further investigation.31

Conclusions

We report the molar absorptivity of TDMA in the IR between 550 cm\(^{-1}\) and 4000 cm\(^{-1}\) and at six temperatures between 352 K and 476 K. Sample emission is eliminated from the measurement using a half-beam block. Increasing the temperature induces significant band broadening. Furthermore, three temperature-dependent peak positions are observed and quantified. The integrated peak areas, however, remain constant across the temperature range. The implications for IR-based process measurements are discussed. In the course of this work, thermal decomposition at 476 K was observed to occur very slowly in contrast to prior results. TDMA thus may be of this work, thermal decomposition at 476 K was observed to occur very slowly in contrast to prior results. TDMA thus may be of this work, thermal decomposition at 476 K was observed to occur very slowly in contrast to prior results. TDMA thus may be

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24. Please see supplemental material at 10.1149/009403jss.

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