The thermal decomposition of tetrakis(ethylmethylamido) titanium (TEMAT) has been investigated in Ar and H\textsubscript{2} gas atmospheres at gas temperatures of 100-400 °C by using Fourier Transform infrared spectroscopy (FTIR) as a fundamental study for the chemical vapor deposition (CVD) of titanium nitride (TiN) thin film. The activation energy for the decomposition of TEMAT was estimated to be 10.92 kcal/mol and the reaction order was determined to be the first order. The decomposition behavior of TEMAT was affected by ambient gases. TEMAT was decomposed into the intermediate forms of imine (C=N) compounds in Ar and H\textsubscript{2} atmosphere, but additional nitride (RC≡N) compound was observed only in H\textsubscript{2} atmosphere. The decomposition rate of TEMAT under H\textsubscript{2} atmosphere was slower than that in Ar atmosphere, which resulted in the extension of the regime of the surface reaction control in the CVD TiN process.

Key Words: Chemical vapor deposition (CVD), Tetrakis(ethylmethylamido) titanium (TEMAT), Titanium nitride, Film, Thermal decomposition

Introduction

Trend in shrinking the size of integrated-circuit (IC) device features leads the continued increase in aspect ratio (depth/diameter) of contacts and vias. Therefore, a conformal process for the deposition of diffusion barrier materials is required for the fabrication of advanced IC devices. Chemically vapor-deposited (CVD) titanium nitride films are widely used for the fabrication of advanced integrated-circuit devices because of their excellent barrier properties, good electrical conductivity, and good step coverage on high-aspect-ratio contact holes and vias. The titanium nitride (TiN) films can be prepared by CVD process using either inorganic or metal-organic precursors. Compared to inorganic-CVD TiN, metal-organic-CVD (MOCVD) TiN is known to have some advantages: low deposition temperature, no chlorine contamination and adequate step coverage on the TiN film are titanium alkyl amides such as tetrakis(dimethylamido) titanium (TDMAT), Ti[N(CH\textsubscript{3})\textsubscript{2}])\textsubscript{4}, tetrakis(diethylamido) titanium (TDEAT), Ti[N(CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}]\textsubscript{4}, and tetrakis(ethylmethylamido) titanium, TEMAT, Ti[N(CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3})\textsubscript{2}]\textsubscript{4}. Among these precursors, TEMAT has not been used widely for CVD TiN compared to TDMAT and TDEAT, although the TEMAT-based CVD TiN films showed better chemical/physical properties than TDMAT or TDEAT-based TiN films. Previously, it was shown that gas-phase chemistry greatly affects the deposition characteristics in the CVD processes. Nonetheless, to our knowledge, there are no reports on the effect of ambient gases on the thermal decomposition of tetrakis(ethylmethylamido) titanium (TEMAT) for CVD TiN process. Therefore, we investigated the thermal decomposition behavior of TEMAT at various gas atmospheres, aiming to relate the gas-phase chemistry and the growth characteristics of CVD TiN films to compare with the decomposition of TDMAT and TDEAT. The gas phase chemical reactions have been mainly studied using in-situ FTIR.

Experimental Section

Materials and Instrumentations. The precursor, TEMAT (99.9%), was purchased from the UP Chemical Inc and used without further purification. There were no detectable impurities in the \textsuperscript{1}H-NMR spectra of the as-received TEMAT. The compound is a yellow-orange liquid with molecular weight of 280.32 g. The density and vapor pressure of TEMAT is 0.95 g/cm\textsuperscript{3} and about 0.4 torr at 60 °C, respectively. The decomposition behavior of the precursor was studied using Fourier Transform infrared spectroscopy (FTIR, Jasco 410 model) by monitoring of the specific chemical bonds, and the schematic drawing of the experimental apparatus is shown in Figure 1. The mixture of carrier gas and vaporized precursor was introduced into a specially designed quartz gas cell (volume: 141.4 cm\textsuperscript{3}), which was covered with a heating block. The precursor container was kept at 55 °C. During the experiment, the gas line from the bubbler to the inlet of cell was heated at 65 °C to prevent precursor condensation. A collimated infrared beam (IR band: 400-4000 cm\textsuperscript{-1}) was irradiated from the FT-IR spectrometer through the quartz cell equipped with two KBr windows, and the passed IR beam was analyzed with a liquid-nitrogen-cooled MCT (Hg-Cd-Te) detector. Each IR spectrum was collected with 8 cm\textsuperscript{-1} resolution and 50 scans.
were averaged. The gas temperature of the cell was measured by K-type thermocouple and varied from 100 to 400 °C under Ar and H₂ gas environments.

The deposition of TiN also carried on the (100) p-type silicon covered by SiO₂ in a low pressure CVD reactor to investigate the effects of ambient gas on the CVD TiN. The films were deposited in the range of 250-375 °C at the total pressure of 1 torr, 55 °C of precursor temperature, and 30 sccm carrier gas. Film growth rate was calculated by dividing the film thickness by reaction time and the thickness of the films was evaluated using scanning electron microscope (Hitachi 5000 SEM model).

Results and Discussion

Figure 2 shows the typical FTIR absorption spectrum of gas phase TEMAT, and the peak assignments are listed in Table 1. The FTIR spectrum of gas phase TEMAT was similar to that of other pure metal alkyl amine compounds. The degree of thermal decomposition of TEMAT was monitored using the intensity of NC₂ asymmetric stretch at 978 cm⁻¹, because the relatively intense NC₂ stretching band is known to be a good signature for the metal[N(CH₃)(CH₃)₄]₄ bond.

Figure 3 shows the IR spectra of TEMAT at cell temperatures of 100, 300, 350 and 400 °C under Ar atmosphere. As can be seen in Figure 3, the peaks intensity of CN₂ asymmetric stretch at 978 cm⁻¹ and of the Ti-N stretch at 603 cm⁻¹ decreased with increasing the cell temperature, suggesting that TEMAT became unstable at a high temperature, causing the decomposition of TEMAT into Ti metal and ethyl-methyl-amine. Here it is interesting to note that the absorption at 1680 cm⁻¹ appeared at high temperatures over 300 °C. This peak could be assigned to the C=N stretching, suggesting that N-CH₃ of TEMAT is

<p>| Table 1. FTIR peak assignments for TEMAT |
|---|---|---|</p>
<table>
<thead>
<tr>
<th>No.</th>
<th>Wave Number (cm⁻¹)</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2962</td>
<td>ν(CH₃)</td>
</tr>
<tr>
<td>2</td>
<td>2929</td>
<td>ν(CH₃)</td>
</tr>
<tr>
<td>3</td>
<td>2841</td>
<td>ν(C-H)</td>
</tr>
<tr>
<td>4</td>
<td>2777</td>
<td>ν(ν(NCH₃))</td>
</tr>
<tr>
<td>5</td>
<td>1452</td>
<td>α(CH₃)</td>
</tr>
<tr>
<td>6</td>
<td>1412</td>
<td>α(CH₃) ; δ(C(CH₃)</td>
</tr>
<tr>
<td>7</td>
<td>1309</td>
<td>δ(NH₃)</td>
</tr>
<tr>
<td>8</td>
<td>1342</td>
<td>δ(C)CH₃ ; α(CH₃)</td>
</tr>
<tr>
<td>9</td>
<td>1297</td>
<td>α(CH₂)</td>
</tr>
</tbody>
</table>

hydride elimination reaction: i.e., Ti[N(C₂H₅)(CH₃)]₄ → CH₃-CH₂-N-CH₂ + Ti[N(C₂H₅)(CH₃)]₃. Likewise, the N-CH₃CH₂ of TEMAT may be also transformed into another imine intermediate by β-hydride elimination reaction: i.e., Ti[N(C₂H₅)(CH₃)]₄ → CH₃-CH₂-N-CH₂ + Ti[N(C₂H₅)(CH₃)]₃. However, the possibility of CH₃-CH₂-N-CH₂ formation could be lower than that of CH₃-CH₂-N=CH₂ formation because of steric reason. Furthermore, the possibility of CH₂=N-CH₂ formation by γ-hydride elimination reaction could be slim because the process requires much higher energy: i.e., Ti[N(C₂H₅)(CH₃)]₄ → CH₂=N-CH₂ + Ti[N(CH₂₃)]₂ N(CH₂₃). The formation of Ti[N=C(CH₃)]₄, a metallacyclic ring compound with CH₃ twist peak at around 1210 cm⁻¹ in TEMAT. Nonetheless, the Ti[N=C(C₃H₇)]₄, a metallacyclic ring compounds, which is the coordinating complex of imine intermediate to the titanium moiety, could be easily formed as observed in the other alkyl amido titanium compounds. The formation of Ti[N=C(CH₃)]₄ also different from the flow type experiment. The decomposition reaction activation energy of 10.92 kcal/mol was obtained from the slope in Arrhenius plot of natural log of TEMAT decomposition rate constant (ln k) vs T⁻¹.

Flow type experiment was used to examine kinetic parameters such as decomposition reaction order and activation energy of TEMAT in gas phase. The decomposition activation energy of TEMAT in the gas phase was obtained by following the method of Yun et al. The gas cell used in this experiment may be considered to be a tubular reactor (plug-flow reactor), in which the reactants are continually consumed as they flow in the reactor. If the reaction is first order, the design equation in the tubular reactor from the mole balance and the rate law at steady state can be written as

\[
\frac{dF}{dV} = -kC \tag{1}
\]

where F is the molar flow rate, \(V\) is reactor volume, \(k\) is the reaction rate constant, and \(C\) is the concentration of the reactant. Integration of Eq. (1) with the inlet concentration of C–C₀ at volumetric flow rate q gives

\[
\ln(C/C₀) = -V/kq \tag{2}
\]

If the plot of \([\ln(C/C₀)]\) as a function of \(-V/q\) is linear with slope \(k\), the reaction order is first order and \(k\) is reaction constant at the temperature. As shown in Figure 4, the plot of \([\ln(C/C₀)]\) for the ratio NC₂ as asymmetric stretching peak as a function of \(-V/q\) is quite linear which suggests that the decomposition reaction is first order. The decomposition rate constant of TEMAT at 375 °C was obtained to be 217.90 m⁻¹ from the slope. The decomposition reaction rate constant of TEMAT was obtained from the slope of the plot temperature \([\ln(C/C₀)]\) vs \(-V/q\) at different gas temperatures from the flow type experiment. The decomposition reaction activation energy of 10.92 kcal/mol was obtained from the slope in Arrhenius plot of natural log of TEMAT decomposition rate constant (ln k) vs T⁻¹.

As the type of the carrier gases was reported to profoundly affect the gas-phase reactions, we evaluated the effect of ambient gas on the decomposition of TEMAT. i.e., the Ar ambient gas was replaced with H₂. To investigate quantitatively the degree of the decomposition of TEMAT at various gas phase temperatures using Ar and H₂ gases, the ratio of the peak intensity of NC₂ asymmetric stretch (I) to CH₂ deformation (I₀) was employed. The reason we adopted the 1369 cm⁻¹ peak of CH₂ deformation peak as a standard was due to the near-insensitivity of this peak under the investigating condition. The peak intensity was obtained by the integration of the peak area, and Figure 5 shows the variation of the peak intensity ratio of I to I₀ at the cell temperatures of 100-400 °C. For all gases, no significant change was found in the ratio of peak intensity upon increasing the temperatures up to 275 °C. However, the ratio greatly decreased at above 300 °C for the case Ar atmo.
sphere, suggesting that the decomposition of TEMAT became significant at above 300 °C. From this results, the gas phase reaction temperature should be kept below 300 °C with Ar to avoid particle generation in Ti(NEtMe)₂-based CVD. On the other hand, significant change of the ratio of peak intensity of NC₂ asymmetric stretching to CH₃ deformation began at 325 °C for the case of hydrogen gas. This indicates that hydrogen suppresses the decomposition reaction of ethylmethylamido groups from Ti(NEtMe)₂. The function of hydrogen gas could be mainly to remove the amide ligand as HNEtMe as seen in the thermal decomposition of TDMAT with SiH₄ gas. This fact was confirmed by ¹H NMR spectroscopy, showing the increased formation of HNEtMe in the H₂ gas atmosphere. Therefore, the hydrogen use would be beneficial for reducing the particle generation in gas phase as well as extension of the controlled regime in Ti(NEtMe)₂-based CVD at the expense of slower decomposition rate of TEMAT.

To observe any spectral changes depending on the ambient gases, FTIR spectra of TEMAT under Ar and H₂ atmosphere were investigated at 375 °C. As can be seen in Figure 6, in the case of H₂ atmosphere, new peak at 2146 cm⁻¹ was interestingly observed along with an imine peak at 1680 cm⁻¹ (C==N) above 350 °C. Since nitrile (RC≡N) compounds usually absorb at 2100-2250 cm⁻¹, we suppose that the peak at 2146 cm⁻¹ might indicate the presence of stable nitrile compound. In the decomposition of TEMAT under argon atmosphere the imine intermediate (CH₃-CH₂-N≡CH₂) could be formed by β-hydride elimination of N-CH₂ as Ti[N(C₂H₅)(CH₃)]₂ → CH₃-CH₂-N≡CH₂ + H-Ti[CH₅(CH₃)-CH₃]. Other type of imine intermediate (CH₃=N-CH(CH₃)₂) could be formed with less possibility due to steric ground by β-hydride elimination of N-CH₃CH₂ of TEMAT as Ti[N(C₂H₅)(CH₃)]₂ → CH₃=N-CH(CH₃)₂ + H-Ti[N(C₂H₅)(CH₃)]. By comparison, unlike the decomposition under argon atmosphere the formation of nitrile intermediate by isomerization of imine intermediate could be promoted by the inter-medacy of Ti≡N-C metallacyclic ring compounds during the decomposition process under hydrogen atmosphere Ti(CH₂-NCH₂CH₃) metallacyclic ring may be isomerized to Ti(NH-CHCH₂CH₃) metallacyclic ring, to H-Ti(NCH₂CH₃), and to H₂Ti[N(CH₂CH₃)]₂ metallacyclic ring. Here hydrogen gas might assist the series of isomerization by providing the coordinating sites for imine and nitrile. The coordinating site could be well prepared by hydrogenolysis of Ti-NEtMe to H-Ti + HNEtMe. The gaseous compounds formed from the thermal decomposition were trapped by bubbling thru NMR solvents. The thermal decomposition of TEMAT in acetonitrile-d₃ (at 70 °C), toluene-d₈ (at 100 °C), and pyridine-d₅ (at 104 °C) was monitored by ¹H NMR spectroscopy. The ¹H NMR spectra clearly showed the formation of HNEtMe from the thermal decomposition of TEMAT on top of many broad and noisy peaks. GC-mass analysis also showed the presence of HNEtMe (molecular ion peak of 59.11).

To evaluate the effect of carrier gases on the film growth, TiN has been grown using a home-made cold-wall type CVD reactor at 250-375 °C in the atmosphere of Ar and H₂ gas. The deposition rate as a function of the substrate temperature is shown in Figure 7. The growth rate of TiN increased with increasing the deposition temperature below 350 °C in all carrier gases. With further increases of substrate temperature, the film growth rate was saturated in Ar atmosphere. However, the film growth rate increased continuously with increasing the substrate temperature in H₂ atmosphere. In addition, the film growth rate with H₂ was higher than that with Ar by 10-20% below 350 °C.

As H₂ has higher thermal diffusivity compared with Ar, we expected that the usage of a higher-thermal-diffusivity gas, H₂, may lead to more decomposition than a lower-thermal-diffusivity, Ar, gas. However, in our experiment, the film growth rate of TiN in H₂ atmosphere increased continuously with increment of the deposition temperature up to 375 °C, in spite of decrements of the film growth rate appearing in Ar atmosphere above 350 °C. Based on the different dependence of film growth rate on the ambient gases and the peak appearance at 2146 cm⁻¹ (C≡N com-

**Figure 6.** FTIR Spectra of TEMAT in gas phase at 375 °C using Ar and H₂ atmosphere.

**Figure 7.** Plot of film growth rate at different substrate temperature.
pounds) only under H$_2$ in Figure 6, it is believed that the decomposition reactions of TEMAT in the gas phase under H$_2$ atmosphere differ from those under Ar gas. We can speculate that hydrogen gas could accelerate the series of isomerization process by providing the empty coordinating sites for imine and nitrile thru the hydrogenolysis of Ti-NEtMe to H-Ti + HNEtMe, although we do not understand at present how H$_2$ is exactly involved in the decomposition reactions. A detailed mechanistic study using several deuterium–labelled TEMAT and proper analytical techniques is in progress and will be published in due course.

Conclusions

As a basic study for TEMAT-based TiN CVD systems, an FTIR study was conducted at the cell temperatures of 100-400°C. The imine intermediate which could be partially transformed by β-hydride elimination reaction of TEMAT was observed in all the tested ambient gases, but the nitrile intermediate was only detected under hydrogen atmosphere at the temperature above 350°C. A plausible mechanism for the sequential isomerization of imine to nitrile by the intermediacy of metallacyclic compounds was suggested. The C≡N peak appearance and the extension of the regime of the surface reaction control in the CVD TiN process clearly show that different reaction pathways could exist under hydrogen ambient and further detailed mechanistic studies should be required to elucidate the decomposition mechanism of TEMAT.

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References