In Situ FTIR Analysis for the Thermal Decompositions of Trimethylgallium and Trimethylgallium-Ammonia Adduct

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The thermal decompositions of trimethylgallium (TMG) and trimethylgallium-ammonia adduct (TMG:NH_3) have been studied using Fourier transform infrared spectroscopy. A static cold-wall reactor is designed for use in the temperature range 25-1000 °C, and the gaseous reactants and products are *in situ* analyzed to obtain the kinetic information. TMG:NH_3 as well as TMG is decomposed around 500 °C with liberation of the CH_3 group. In the case of TMG:NH_3, the CH_3 group abstracts hydrogen from NH_3, forming CH_4. The decomposition of NH_3 can be described as second-order kinetics, and that of TMG and TMG:NH_3 as first-order kinetics. The decomposition rate constant of TMG:NH_3 at 1.6 Torr is estimated to be $\log k_1 = 15-63\ (\text{kcal/mol})/2.303RT$.

Introduction

Chemical vapor deposition (CVD) is now a leading technique for the epitaxial growth of inorganic materials such as III/V semiconductors. Among these, gallium nitride (GaN), which has a bandgap of 3.4 eV, is expected to be used as a blue-emitting diode material. For the epitaxial growth of GaN, trimethylgallium (TMG) and ammonia (NH_3) are most frequently used as starting materials. These are often mixed in the gas phase prior to their passage over a heated substrate of about 1000 °C.[1] For improvement of the epitaxial growth of GaN, it is important to understand how the reactions take place during the CVD process. The mechanism involved in the CVD of GaN, however, is very complicated, and there is much disagreement among researchers on the thermal decomposition mechanism of TMG.

The thermal decomposition of TMG was first studied in a toluene flow system by Jacko and Price.[2] They proposed the stepwise mechanism, in which the first and the second methyl groups were liberated as radicals, the monomethylgallium being condensed into polymeric solid on the reactor wall. Later studies were also performed under the experimental conditions similar to those of CVD reactors. In almost all cases, the thermal decomposition of TMG in H_2 and N_2 atmosphere was found to give off CH_4 as a major form of hydrocarbon debris,[3,4] while no $GaCH_3$ polymer was found. DenBaars et al.[5] reported that only two CH_4 molecules were generated in a H_2 atmosphere from each TMG molecule below 460 °C. However, at higher temperatures all three methyl groups were given off as CH_4.

There are conflicting reports concerning the effects of carrier gases on the decomposition reaction. Yoshida et al.[4] stated that in a hot-wall reactor the thermal decomposition of TMG took place at 450 °C in H_2 atmosphere, but in N_2 atmosphere the same occurred at 550 °C. On the other hand, Lee et al.[6] and Mazzarese et al.[7] in their low-temperature studies found no difference in product formation between H_2 and N_2 atmospheres. The thermal decomposition of TMG can be affected by many subtle factors, such as pressure,[8,9] catalytic effect of surface,[10,11] and reactor type.[12]

Another important aspect in CVD process of GaN synthesis is the formation of adduct between TMG and NH_3. The adduct of a TMG:NH_3 type is formed even at room temperature during the gas-phase mixing step, where TMG acts as Lewis acid and NH_3 acts as Lewis base. Sywe et al.[13] found the rate constant of the adduct formation to be 5.89×10^{-3} Torr^{-1} s^{-1} at 150 °C. When TMG:NH_3 was heated at 120 °C under 450 Torr of nitrogen, it was condensed into the trimer $[(CH_3)_2Ga{:}NH_2]_3$ containing a $(GaN)_3$ ring, with liberation of CH_4.[14]

In this paper, the thermal decompositions of NH_3, TMG, and TMG:NH_3 in a static cold-wall reactor have been studied by the Fourier transform infrared (FTIR) spectroscopy. The *in situ* FTIR analysis can detect the infrared-active reactants and products present in the gas phase at the experimental temperatures. This permits continuous observations of the irreversible reaction pathways, hence making it possible for the first time to

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determine the rate constant of the thermal decomposition of TMG:NH_3 at 520 and 550 °C.

Experimental Section

For measurement of high-temperature FTIR spectra the gas cell was constructed of a stainless steel hexagonal-port chamber with two NaCl windows attached in parallel. Viton O-rings were inserted between the windows and the flanges. The inner diameter of one port was 3.0 cm, and the length between two NaCl windows was 13.5 cm. A tantalum resistive heater with dimension of 30 × 5 × 0.1 mm^3 was positioned at the center of the chamber. While the O-rings were kept below 100 °C, the temperature of the heater can be elevated up to 1100 °C. Gas handling lines and Baratron gauge were connected to the cell. The temperature of Ta surface is measured by means of a K-type thermocouple, which is taken as a reaction temperature in the present discussion.

A DIGILAB Model FTS-20/80 FTIR spectrometer was used to collect the infrared spectra. The cross-sectional diameter of the IR beam was about 2 mm. The spectral resolution was 2 cm^{-1} for the compound identification at each heater temperature and 8 cm^{-1} for the kinetic analysis. The IR beam was allowed to pass the region just 0.5 cm above the heater. TMG (99.9999%) from Strem Chemicals and NH_3 (99.999%) from Matheson were used without further purification. To obtain IR spectra as a function of temperature, the initial pressure investigated was adjusted to about 2.5 Torr for NH_3 and TMG. The spectra of pure TMG decomposition were compared with those of TMG decomposition in H_2 and NO atmosphere. When TMG and NH_3 were mixed, the total pressure decreased until formation of the TMG:NH_3 adduct became complete. Therefore, when NH_3 was introduced into the vessel having previously filled with TMG, the minimum reading on the pressure gauge was taken as the initial pressure of TMG:NH_3. When 2.6 Torr of TMG was used, the initial pressure of the mixture was found to be 1.6 Torr.

The kinetic data were obtained from the relative absorbance of the peak characteristic of the compound decomposition. The partial pressures of NH_3, TMG, and TMG:NH_3 were derived from the IR absorption bands observed at 968, 585, and 561 cm^{-1}, respectively. Without filling any atmospheric gas, the IR intensities for NH_3, TMG, and TMG:NH_3 were measured at a given temperature as a function of time under the initial pressures of 1.2–40 Torr, 1.4–4.0 and 1.6 Torr, respectively. Assuming that Beer's law is valid within the region of the experimental conditions, calibration was made by plotting IR absorbance against the pressure of each gas at a given temperature.

Results and Discussion

The IR spectra of NH_3 as a function of experimental temperatures are shown in Figure 1. Three vibrational modes are IR active in the region of 500–3500 cm^{-1}. It is noted that the peaks between 1400 and 1800 cm^{-1} are due to atmospheric humidity outside the cell and not completely substracted. The band at 3334 cm^{-1} is due to N–H symmetric stretching and that at 1628 cm^{-1} to N–H asymmetric deformation. The peaks at 968 and 931 cm^{-1} are assigned to the inversion doubling of the symmetric deformation. They are in good agreement with the data published previously.[15] When the temperature reaches 900 °C, NH_3 is found to be decomposed completely.

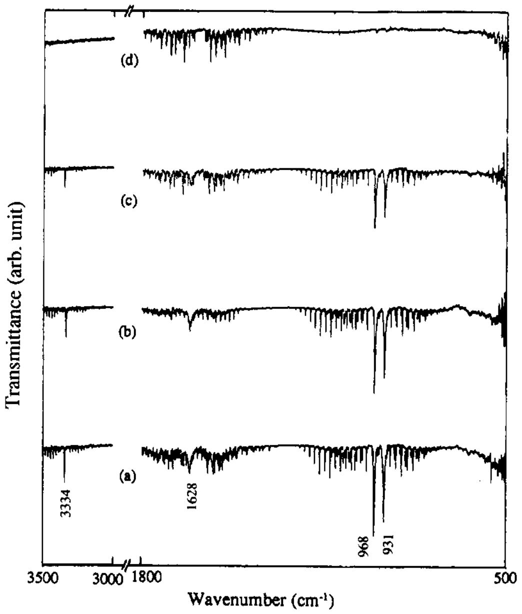

Figure 1. IR spectra of NH_3 at (a) 25, (b) 400, (c) 800, and (d) 900 °C.

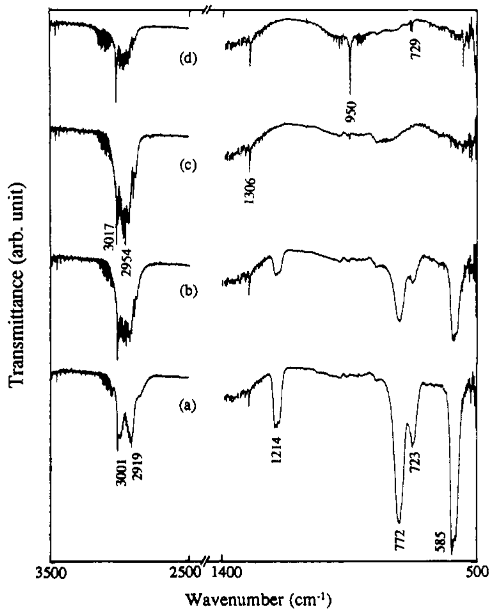

Figure 2. IR spectra of TMG at (a) 25, (b) 500, (c) 600, and (d) 1000 °C.

Figures 2 and 3 show the IR spectra of TMG and TMG:NH_3 during respective thermolysis. The spectral peaks obtained at the room temperature are assigned in Table1. It is seen that due to the adduct formation, the frequency of the CH_3 symmetric deformation is substantially shifted to the lower region of the vibrational energy. The frequency shift appears to result from the change of the molecular symmetry from D_{3h} of TMG to C_{3v} of TMG:NH_3. In both cases, all the peaks responsible for organometallic compounds disappear gradually at 500 °C. Simultaneously, it is observed that the CH_4 peaks increase at 3017 and 1306 cm^{-1} and the C_2H_6 peaks increase in the vicinity of 2954 cm^{-1}. At 600 °C, both TMG and TMG:NH_3 were decomposed completely.

Upon complete decomposition of TMG at 1000 °C, the intensities of C_2H_6 bands decrease with the appearance of new peaks at 950 and 729 cm^{-1}, as shown in Figure 2d. Nishizawa et al.[17] stated that these peaks were attributable to the decomposition of CH_4 at 930 °C. When C_2H_6 alone was heated in the gas cell, however, similar phenomena appeared at 1100 °C and the bands at 950 and 729 cm^{-1}

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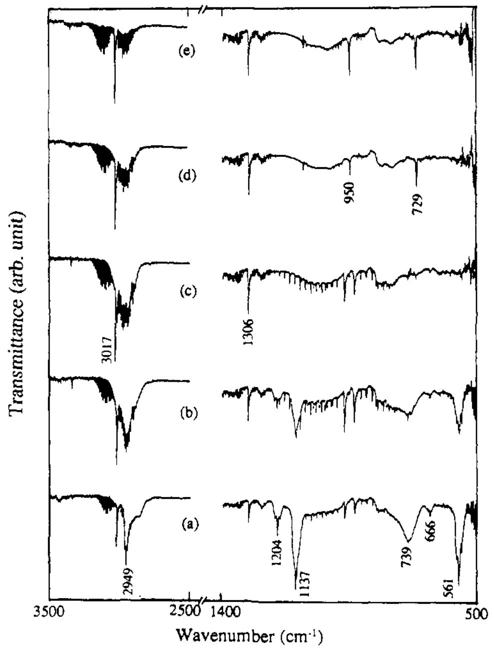

Figure 3. IR spectra of TMG:NH_3 at (a) 25, (b) 500, (c) 600, (d) 900, and (e) 1000 °C.

Table 1. Frequencies for the Normal Vibrations of TMG and TMG:NH_3 (cm^{-1})[a]

TMG	TMG:NH_3	assignment[13,16]
3001 m	2949 m	CH_3 asymmetric stretching
2919 m		CH_3 asymmetric stretching
2852 sh, b		overtone(2 × CH_3)
	1212 m, sh	NH_3 symmetric deformation
	1204 m	NH_3 symmetric deformation
	1196 m, sh	NH_3 symmetric deformation
1214 s	1137 s	CH_3 symmetric deformation
1206 m, sh		CH_3 symmetric deformation
1200 m, sh		CH_3 symmetric deformation
772 s	739 m, b	CH_3 rocking
723 m	666 w	CH_3 rocking
	567 s, sh	Ga–C_3 stretching
585 s	561 s	Ga–C_3 stretching
581 s, sh	550 s, sh	Ga–C_3 stretching
577 s, sh		Ga–C_3 stretching
572 s, sh		Ga–C_3 stretching

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; b, broad.

were identified as C_2H_4 and C_2H_2, respectively. In the case of TMG:NH_3, as shown in Figure 3d, C_2H_6 is decomposed at 900 °C and the band due to C_2H_2 is somewhat intensified.

As shown in Figure 4, the intensity of the band due to C–H stretching of C_2H_6 tends to vary with the surrounding atmospheric gases. When only TMG is filled in the reactor, the main products of the thermal decomposition at 600 °C are found to be CH_4 and C_2H_6. When TMG is decomposed thermally in H_2 and in a radical scavenger like NO, the band intensity of C_2H_6 decreases remarkably. This implies that the production of radicals during the thermal decomposition plays an important role for the reaction process. The exact scheme involving free radicals,[18] however, cannot be detailed here, since the decomposition of ethane may proceed in rather complicated manners via numerous steps, such as disproportionation, termination, etc., which are beyond the scope of the current work. The formation reaction of C_2H_6 may be expressed simply as

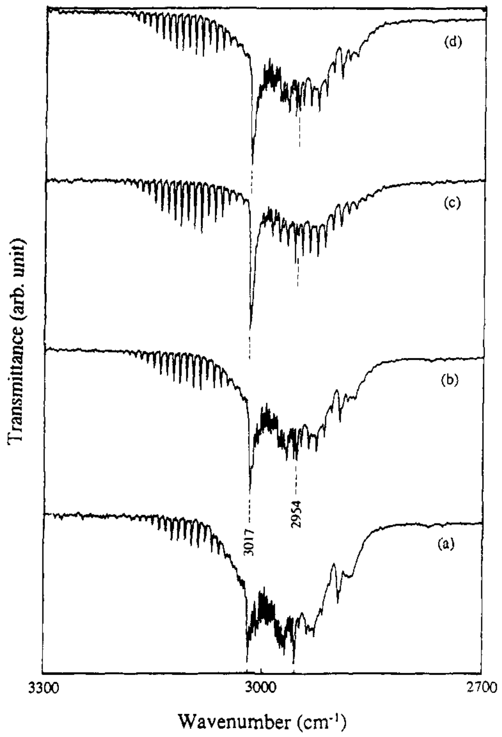

Figure 4. Fine structures of C–H stretching region at 600 °C of (a) TMG, (b) TMG in H_2, (c) TMG in NO, and (d) TMG:NH_3.

$$CH_3 + CH_3 \xrightarrow{k_2} C_2H_6 \qquad (1)$$

This permits the rate of ethane production to be generalized in terms of the bimolecular kinetics, which is proportional to the square of the CH_3 radical, $\upsilon = k_2[CH_3]^2$, where υ is the reaction rate and k_2 is the rate constant. Thus the low intensity of the bands due to C_2H_6 reflects a low steady-state concentration of CH_3 radicals in H_2 and NO atmospheres. The spectrum of TMG:NH_3 system at 600 °C is very similar to that of TMG in H_2 atmosphere. This indicates that TMG:NH_3 decomposes in a manner similar to the TMG decomposition, liberating CH_3 groups, and that NH_3 acts as a hydrogen donor with respect to the CH_3 groups generated during the thermal decomposition of TMG.[7]

Decomposition kinetics were measured in a cold-wall reactor. However, the reaction pathway can be altered with respect to the reactor type in use, such as cold-wall reactor or hot-wall reactor.[12] By means of the former reactor, the temperature gradients can change the reaction rates. The more the ratio of the heater to the reactor volume, the faster the reaction rate is observed. However, it is assumed that the activation energy and the kinetic order should be affected very slightly by the temperature gradient, because they depend only on intrinsic factors such as bond energies, molecular shapes, and activation and relaxation pathways.

The kinetic data were interpreted with the assumption that the decomposition occurred only in the gas phase. When the heater interacts with the reactant,[10,11] the surface-catalyzed reaction must be considered. In this case, the rate constant can be written after Hoshino's expression:[9]

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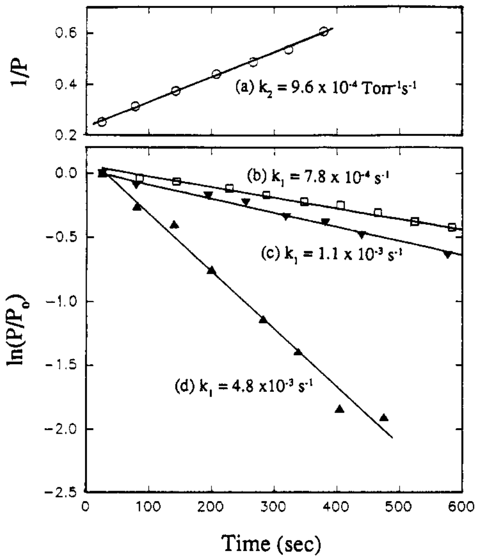

Figure 5. Kinetic data for (a) 3.95 Torr of NH_3 at 830 °C, (b) 2.17 Torr of TMG at 550 °C, and 1.6 Torr of TMG:NH_3 at (c) 520 °C and (d) 550 °C. P and P_0 are partial pressure and initial pressure of reactant, and k_1 and k_2 are first- and second-order rate constants, respectively.

$$k_{\text{obs}} = k_g + k_s A \frac{K_s}{1 + K_s P} \tag{2}$$

where k_g and k_s are the decomposition rate constants in the gas phase and on the surface, respectively. A and K_s are the surface concentration and the adsorption–desorption equilibrium constant at the heater surface, and P is the TMG partial pressure in the gas phase. During the experiment, however, no pressure decrease caused by the adsorption of the reactants onto the Ta heater was observed, so that $K_s = 0$. Therefore, the second term in eq 2 can be ignored and the decomposition in the gas phase can be justified.

The results of the kinetic assessment are shown in Figure 5. It appears that the decomposition of NH_3 follows a second-order reaction, while TMG and TMG:NH_3 are decomposed in first-order kinetics. In terms of the Lindemann theory,[19] the unimolecular reaction is accounted for, which may proceed with the following three steps:

$$\text{activation:} \qquad A + A \xrightarrow{k_a} A^* + A \tag{3}$$

$$\text{deactivation:} \qquad A^* + A \xrightarrow{k_d} A + A \tag{4}$$

$$\text{conversion:} \qquad A^* \xrightarrow{k_c} \text{products} \tag{5}$$

where A and A* are reactant and its activated species, and k_a, k_d, and k_c being the rate constants for collisional activation, deactivation, and conversion into products, respectively. When the collision energy becomes localized in a particular bond, A* can be converted into products. The overall rate (v) for the above three reactions under steady-state conditions is then described as

$$v = k_c[A^*] = \frac{k_c k_a P_A}{k_c + k_d P_A} P_A \tag{6}$$

If the deactivation rate is negligible in comparison with the conversion rate, $k_c \gg k_d P_A$, then the unimolecular reaction rate becomes dependent on the square of the reactant pressure, P_A^2. When the case is reversed, $k_d P_A \gg k_c$, the overall reaction kinetics becomes a first order. The molecule composed of a large number of atoms, however, can store the excess energy in many vibrational degrees of freedom. Thus it tends to have the low chance of isolating a sufficient amount of energy in the vibrational mode necessary to break a particular bond. Consequently, there is a strong tendency for k_c to be lower in the large molecule.[20] Therefore, the first-order kinetics for TMG and TMG:NH_3 can be explained in such a way that their activated species may be of the conversion rate much slower than the deactivation rate. In addition, the second-order kinetics for NH_3 indicates that the conversion of its activated species goes on much faster than the deactivation.

As in Figure 5c,d, the plots of $\ln(P/P_0)$ vs time are obtained for TMG:NH_3 decomposition at two different temperatures. From the Arrhenius relation, the rate constant is written as

$$\log k_1 = 15 - \frac{63 \text{ kcal/mol}}{2.303RT} \tag{7}$$

The activation energy of 63 kcal/mol for TMG:NH_3 appears to be similar to the reported value for TMG.[9,21] According to the *ab initio* molecular orbital method,[21] the frequency factor is calculated to be $10^{16.3}$ s^{-1} for a simple bond dissociation to radicals. Thus the value of 10^{15} s^{-1} in eq 7 indicates that TMG:NH_3 liberates CH_3 radicals during the thermal decomposition.

Conclusions

In a static cold-wall reactor, both TMG and TMG:NH_3 start to decompose at about 500 °C and the main gaseous products are CH_4 and C_2H_6. The C_2H_6 formed after metalorganic decomposition goes to C_2H_4 and C_2H_2 at higher temperatures.

The thermal decompositions of NH_3, TMG, and TMG:NH_3 can be best described in unimolecular reactions. TMG and TMG:NH_3 show first-order kinetics, whereas NH_3 follows second-order kinetics. These can be explained by relative activation and deactivation rates of respective molecules. From the Arrhenius-type expression, the activation energy for TMG:NH_3 decomposition is determined to be 63 kcal/mol. The frequency factor, 10^{15} s^{-1}, for the adduct decomposition indicates that the CH_3 group is generated as the intermediate species during the adduct decomposition under the experimental range of pressure.

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