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IN SITU MECHANISTIC STUDIES OF MOCVD GROWTH OF III/V SEMICONDUCTORS

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ABSTRACT

Our initial studies of metal-organic chemical vapor deposition for the growth of III-V semiconductors have developed in situ techniques to follow the growth process both in the gas phase and in the on the surface (in the sorbed state). The results have provided a more direct perspective of the mechanisms and kinetics of the reaction between group V alkyls and group III hydrides. Both Fourier transform infrared spectroscopy (FTIR) and detailed surface spectroscopy have been employed to study the course of the reaction and the nature of the solid products. We conclude that the crucial steps of the reaction occur on the surface of the solid substrate. Although gas phase decomposition of the group V organometallic occurs, the reactions leading to the formation of III-V bonds proceed on the surface. This leads us to focus on the availability of adsorbed atomic hydrogen as it relates to the removal of alkyls from the group V metal organic in the continuation of this research.

BACKGROUND

TMGa and ammonia were chosen in our initial studies for several additional reasons. TMGa is a common MOCVD growth source and thus is readily available in electronic grade purity; further, the kinetics of decomposition have been well characterized(1,2,3) and the IR spectra have been studied in detail(4,5). Ammonia was chosen as the group V source (it is a well characterized, reactive molecule and deuterium labeled isotopes are readily available). In addition to gaining insight into the formation of GaN, AlN and the ternary compound, we believe that the findings may be directly related to other MOCVD reactions to produce other III/V semiconductors (e.g., GaAs). Implied by this approach is the assumption that the reaction mechanisms involving ammonia are similar to those of arsine and phosphine so that meaningful comparisons can be made. We recognize that this has yet to be demonstrated.

Three techniques were employed for our initial studies: in situ gas phase Fourier transform infrared (FTIR) spectroscopy, detailed surface analysis of the deposited film (including: Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and electron dispersive spectroscopy (EDS)), and in situ surface infrared spectroscopy employing attenuated total reflectance (ATR). This information was then used to address

the controversial issue of whether the organometallic and group V hydride pyrolyze before they react(6,7) or react directly with each other(8), and if the primary reactions are gas phase or surface catalyzed.

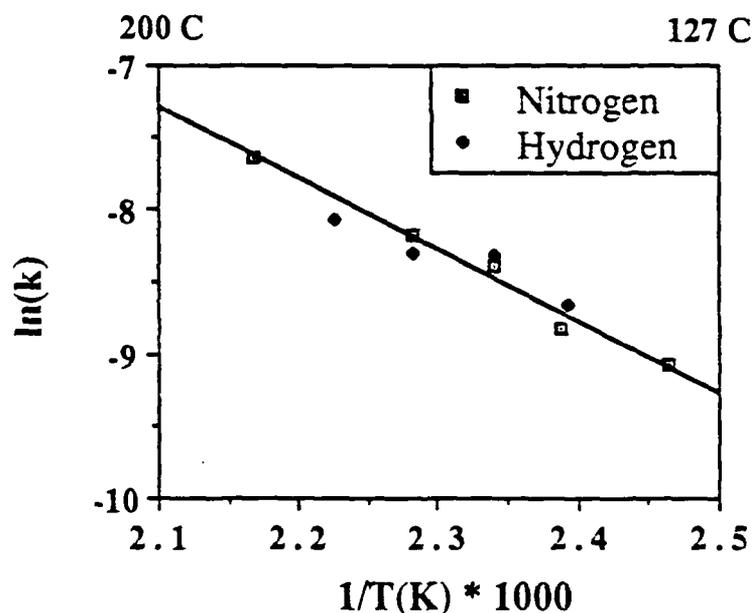
In situ FTIR analysis was used to detect directly the reactants and products present in the gas phase or on a surface; further, it may be able to identify intermediate reaction species. It has the potential of monitoring the rate of disappearance and/or production of these species and thereby permits us to analyze the reaction kinetics. By using deuterium labeled compounds, we were able to study the reaction pathway by tracing specific groups of hydrogen in the reaction.

RESULTS

IN SITU GAS PHASE STUDIES

For the gas phase analysis a special gas cell was designed by us and built by Harrick Scientific. The cell as described was designed to operate up to 300°C. This reactor was placed in the sample path of a Nicolet 7199 FTIR spectrometer. The spectrometer used a liquid nitrogen cooled MCT detector and a KBr beam splitter. As configured the spectrometer could sample in the spectral range of interest, 3500-400 cm^{-1} .

The similarity of decomposition rates in nitrogen and hydrogen are apparent in the figure below where the results are displayed on an Arrhenius plot. Here the rate of reaction was examined over a variety of temperatures in both nitrogen and hydrogen.



Although the rate was the same in both N_2 and H_2 carrier gases, the gas phase products changed. This suggests that the rate limiting step for decomposition is the breaking of the Ga-C bond to form the methyl radical, rather than a reaction with the carrier gas. Other studies have shown the TMGa decomposition rate is first order in TMGa(1,2,9), but the results on the effect of the carrier gas on TMGa decomposition differ. Others found that the decomposition takes place faster and at a lower temperature in a hydrogen carrier gas. From this data they concluded that hydrogenolysis was the primary reaction pathway. In a non-isothermal reactor a substantial thermal gradient may exist. The temperature profile, and therefore the reaction rate, depends on the rate of heat transfer from the reactor walls. This is a strong function of the thermal conductivity of the carrier gas. Nitrogen and hydrogen have substantially different thermal conductivities. We estimate that for the system used by Yoshida et al.(1) the isothermal decomposition rates would be the same in either nitrogen and hydrogen. Our in situ isothermal reactor eliminated this effect.

Very little CH_3D was produced for the TMGa decompositions done in deuterium. This is consistent with the results of Schlyer and Ring for decomposition of TMGa in a vacuum(10). Our results suggest the methyl radicals in a N_2 ambient are etching the surface of the silicon substrate. We detected infrared bands characteristic of alkyl-silicates. They may be the result of methyl radicals reacting with silicon oxide from wafers placed in the gas cell, since silicon samples placed in the IR cell could not be heated to $800^\circ C$ in hydrogen to remove any surface oxide. For samples that were exposed to the high temperature hydrogen, there was a preferential deposition of gallium in the etched pits on the silicon surface. Both the formation of alkyl-silicates and the etching of a silicon surface by TMGa have been reported previously(11).

Gas Phase Reaction of TMGa & NH_3

When TMGa and ammonia were mixed at temperatures below $100^\circ C$ a viscous clear liquid product formed. This made it necessary to preheat the carrier gas to $100^\circ C$. This limited our study of the reaction between TMGa and ammonia to temperatures above $100^\circ C$. The carrier gas was preheated to $100^\circ C$ to stop the formation of $TMGa \cdot NH_3$. It was determined that little or no adduct was present by comparing our spectra to published results for the infrared spectra of the adduct(12). This indicates that if the adduct were present the concentration was less than could be detected.

Methane is formed faster when TMGa reacts with ammonia. At $100^\circ C$ the increase in methane generation is 1.4 times the rate when TMGa is decomposed in the carrier gas alone. The other noticeable change is that the amount of ammonia in the gas phase decreases with time.

When ND_3 is used instead of NH_3 , predominantly CH_3D is formed instead of CH_4 . This is based on a 1:3 ratio for the infrared absorbance at 2200 and 3020 cm^{-1} , and the absence of any unidentified peaks in the 950-1100 cm^{-1} range.(13,14). This suggests that the methyl groups from the TMGa (possibly as radicals) react easily with the hydrogen from the ammonia. Also, since methane is produced faster when ammonia is present, we conclude that the components react with each other rather than decomposing separately followed by recombination of the fragments as shown in the equation below. This reaction may take place on the surface or in the gas phase, but our internal reflectance studies below indicate that the reaction is taking place on the surface.

SURFACE ANALYSIS

To better understand the morphology and composition of the deposited films, a special reactor was designed. The reactor was a 24" piece of 1/4" 316 stainless steel tubing with VCR fittings on either end. This tube was placed in a 14" horizontal ceramic tubular furnace capable of temperatures up to 1000°C. A small Si (111) n-type wafer with p-type epitaxy was placed in the center of this reactor.

SEM's and EDS's of TMGa Decomposition

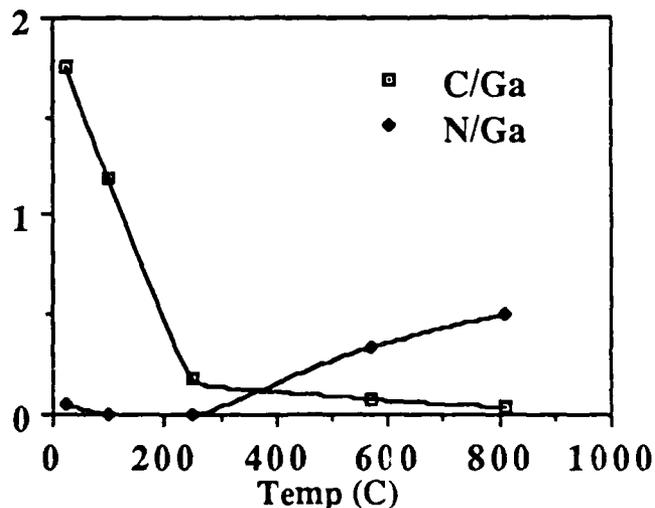
The difference between hydrogen and nitrogen carrier gases is most noticeable on the surface. For the decomposition in hydrogen the surface is smooth with occasional droplets of gallium. Under the same conditions only switching the carrier gas to nitrogen the surface is actually etched by the TMGa as it decomposes. EDS shows preferential deposition of Ga in these pits.

To show that ammonia, rather than N_2 , is required for MOCVD growth of GaN we examined deposited films on silicon substrates for TMGa decompositions in nitrogen at 200, 570 and 810°C. The morphology changed considerably with temperature. At 570°C balls of gallium formed, while at 810°C fingers of gallium covered the surface. In no case was any nitrogen detected on the surface.

Surface Analyses of the Reaction

We analyzed the the reaction products on the surface of the Si crystals exposed to TMGa and ammonia at the same time. We looked at both the effect of V/III ratio at one temperature, and the effect of temperature at a constant V/III ratio.

AES analysis of the silicon samples showed some general trends. As shown below, carbon incorporation decreased as the V/III ratio increased at 250°C. One should note that under these conditions (<300°C) no nitrogen was incorporated in any of these films.



The effect of temperature on carbon and nitrogen incorporation into the deposited material as measured by AES.

At 100°C the silicon substrate was etched. Methyl radicals are formed during the decomposition of TMGa. These radicals have been observed in the gas phase(15). But they are highly reactive, thus have a short lifetime. Hydrogen may dissociate on the surface and combine with surface methyl radicals preventing reactions with the Si substrate when decompositions take place in hydrogen. We are not sure why less gallium is found on the surface after decompositions in hydrogen than after identical conditions in nitrogen, but our results do indicate that the final step(s) in the decomposition is taking place on the surface. Further, the difference between the surfaces after a TMGa decomposition in hydrogen or nitrogen can be attributed to surface hydrogen participating in the decomposition.

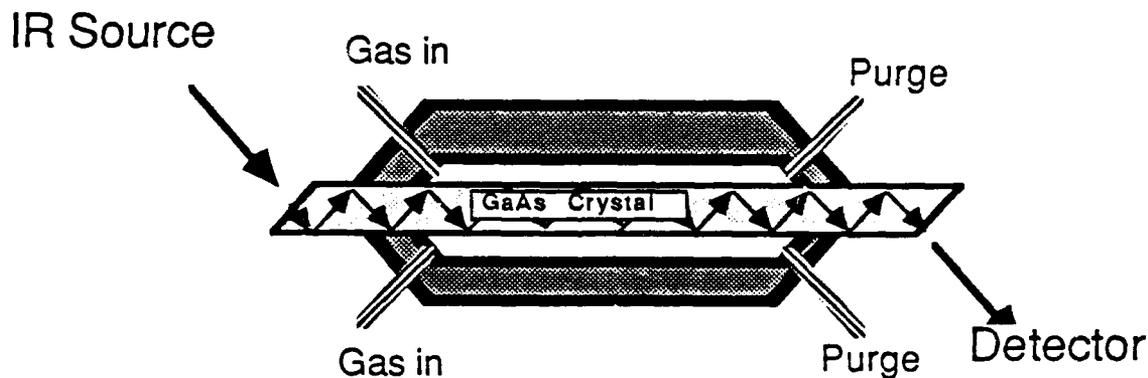
We also examined the deposition products that were formed by heating TMGa in N₂ atmosphere to temperatures of 570 and 810°C. Essentially no nitrogen was found in the deposits and the morphology differed dramatically from those obtained using NH₃. This shows that the reaction involving NH₃ is significantly different than the one involving its decomposition product, gaseous N₂. This shows the importance of the N-H bonds for the formation of GaN. The lack of nitrogen on the surface of Si substrates at 100 and 212°C gives some insight into the surface reaction. At 250°C the presence of ammonia reduced the amount of carbon deposited in the film even though no nitrogen was incorporated. The ammonia decomposition may produce adsorbed hydrogen as well as

gaseous nitrogen. The hydrogen is free to react with the methyl radicals which helps prevent carbon incorporation in this temperature range.

At 570 and 810°C nitrogen is incorporated into the solid. This is consistent with published data for the MOCVD growth of GaN(15-17). Reaction between TMGa and ammonia may or may not result in the formation of GaN. If it forms, a Ga-N bond must be formed before a N-N bond.

IN SITU INFRARED SURFACE ANALYSIS USING ATR

A novel technique was developed in order to study the surface MOCVD reaction. We used ATR to analyze the infrared spectra of the adsorbed species during the adsorption and reaction of NH_3 with TMGa. In ATR light is reflected at the external surface from within a transparent single crystal. This is represented below in the schematic for the reactor employed in our studies. GaAs was used as the internal reflection element, IRE. It is transparent in the infrared across most of the infrared frequency range and should provide a reactive surface for epitaxial III-V MOCVD growth. As the light is reflected several times (50-100 in our experiments) from the external surfaces, the light is attenuated by adsorption due to any species present on the surface. The adsorption spectrum is analyzed as in conventional infrared spectroscopic techniques, in our studies by FTIR.



ATR cell for in situ study of MOCVD on a GaAs surface

Numerous experiments were conducted to analyze the sorption of the reactants and their reaction on the GaAs surface. Moreover, three different GaAs surfaces were employed in these studies: 100, 111(A) and 111(B). They differ in their exposed Miller indexed planes (100 vs 111) or in the dominant species present on the surface (Ga for 111[A] and As for 111[B]). Further, we find a competition between the adsorption of

NH₃ and TMGa. As a consequence if TMGa is first adsorbed onto the surface, the sorption/ decomposition of NH₃ is inhibited and the rate of dealkylation of TMGa is severely quenched. It is apparent that both the hydride and the metal organic must gain access to the surface in order that the hydride is able to decompose and to assist in the decomposition of the metal organic. These studies confirm the results of the gas phase and solid surface analyses described above: **a crucial portion of MOCVD growth at lower temperatures is the surface catalyzed reactions between an adsorbed metal organic and the sorbed atomic hydrogen formed from the decomposition of the metal hydride.** There are several implications of this in terms of optimizing and improving the yield of III-V growth by MOCVD and these will be studied in our continuing research.

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PRESENTATIONS & PUBLICATIONS

There have been several presentations and publications resulting from our initial studies. These are listed below.

Presentations

D. Mazzaresse, A. Tripathi, W.C. Conner, K.A. Jones, L. Calderon and D.W. Eckart. *An In Situ FTIR Study of the Reaction Mechanisms Between TMG and NH₃*. Third Biennial OMVPE Workshop, Brewster, MA, Sept. 1987.

D. Mazzaresse, A. Tripathi, W.C. Conner, K.A. Jones, L. Calderon and D.W. Eckart. *In Situ FTIR and Surface Analysis of the Decomposition of, and Reaction Between TMGa and Ammonia*. 1988 Electronic Materials Conference, Boulder CO, June 1988.

A. Tripathi, D. Mazzaresse, W.C. Conner and K.A. Jones. *A Study of the Adsorption of Ammonia and TMGa on GaAs and the Surface Reaction Between Them Using Internal Reflectance Spectroscopy*. To be presented in Atlantic City, N.J., Oct. 1988.

Publications

D. Mazzaresse, A. Tripathi, W.C. Conner, K.A. Jones, L. Calderon and D.W. Eckart. *In Situ FTIR and Surface Analysis of the Decomposition of, and Reaction Between TMGa and Ammonia*. Accepted for publication in the Journal of Electronic Materials.

A. Tripathi, D. Mazzaresse, W.C. Conner and K.A. Jones. *A Study of the Adsorption of Ammonia and TMGa on GaAs and the Surface Reaction Between Them Using Internal Reflectance Spectroscopy*. J. Electronic Materials 18-1, 45 (1988)