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Mechanism of the photochemically induced reaction between $Ga(CH_3)_3$ and HN_3 and the deposition of GaN films

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Gaseous HN_3 reacts with surface-bound $Ga(CH_3)_x$ species slowly at 300 K to produce thin films containing azide-substituted gallium compounds. When mixtures of HN_3 and $Ga(CH_3)_3$ over the surface are irradiated at 253.7 nm, the reaction is dramatically accelerated, and films containing GaN and complexed N_2 are produced. Heating of these films to 400 K drives off the N_2 leaving GaN. The mechanism of the reaction is thought to involve photodissociation of HN_3 to produce excited $NH(a^1\Delta)$ and N_2, followed by insertion of the $NH(a^1\Delta)$ into the Ga–C bond of surface-bound $Ga(CH_3)_x$ molecules. The insertion product eliminates CH_4 to leave GaN. © *1998 American Institute of Physics.* [S0003-6951(98)02301-8]

A number of laboratories have reported the successful use of azides in the low temperature deposition of nitride thin films. In particular, HN_3 has been used as a reagent in the chemical vapor deposition (CVD) of films of BN,[1] InN,[2] and GaN.[3] Very recently, researchers at Emory University demonstrated[4] the production of high quality GaN films from the reaction of HN_3 with $Ga(C_2H_3)_3$at 873 K. Research in our laboratory[5,6] has explored the mechanisms of the room temperature reactions of HN_3 with BCl_3 and $Al(CH_3)_3$. The gas phase reaction of HN_3 with BCl_3 was shown[5] to proceed quantitatively to $B(N_3)_3$ and HCl. $B(N_3)_3$ is an energetic molecule which decomposes either thermally or upon photolysis in the UV to produce BN films. A similar addition-elimination reaction occurs[6] between HN_3 and $Al(CH_3)_3$ to generate $Al(N_3)_3$ and CH_4. The $Al(N_3)_3$ condenses as a film at 300 K, and gentle heating to 400 K drives off the excess N_2 leaving a film of AlN. In this letter, we report the results of experiments which explored the reaction between HN_3 and $Ga(CH_3)_3$ at 300 K and under irradiation with a low pressure Hg lamp.

The experiments were performed with the apparatus which has been described previously.[5,6] The reagent gases [a 10% mixture of HN_3 in He and $Ga(CH_3)_3$]were handled in a stainless steel vacuum system. The HN_3 was prepared by the reaction of NaN_3 with stearic acid at 400 K; $Ga(CH_3)_3$ was obtained from Morton Metalorganics. The gases were mixed in either stainless steel or fused silica reactors which were equipped with KCl windows for analysis by Fourier transform infrared (FTIR) absorption spectroscopy. The fused silica reactor allowed the gases to be irradiated during the progress of the reaction with a low pressure Hg lamp (4.5 mW/cm^2 at 2.5 cm). The UV output of the lamp is dominated by the 253.7 nm Hg line. Radiation at this wavelength is known to dissociate HN_3 to electronically excited $NH(a^1\Delta)$ and N_2 with a quantum yield near unity.[7] The reaction vessels required extensive passivation with the $Ga(CH_3)_3$ reagent prior to admission of HN_3 to the system. Reaction of the $Ga(CH_3)_3$ with the reactor walls (either stainless steel or fused silica) was found to generate CH_4, observed by IR absorptions at 3018 and 1306 cm^{-1}. The rate of production of CH_4 declined to near zero as successive samples of $Ga(CH_3)_3$ were admitted to the system and pumped off. We believe that the passivation process involves reaction with hydrogen-bearing moieties on the walls, resulting in the liberation of CH_4 and a layer of $Ga(CH_3)_x$ ($x=1$ or 2) bound to the walls. HN_3 was admitted to the system only after passivation was complete.

Various amounts of HN_3 were added to 3.0 Torr pressures of $Ga(CH_3)_3$, up to HN_3: $Ga(CH_3)_3$ ratios of 4:1. While there was evidence of reaction [loss of the HN_3 and $Ga(CH_3)_3$ initially present, as shown by the IR spectra of the gas mixtures], there was no clear stoichiometry of the kind that was observed[5,6] in the HN_3 reactions with BCl_3 or $Al(CH_3)_3$. Further, the reaction was extremely slow and proceeded at the same rate when gaseous $Ga(CH_3)_3$ was not present; i.e., virtually all of the reaction occurred between HN_3 and the $Ga(CH_3)_x$ species in the passivation layer on the vessel walls. The IR spectrum of the products of the reaction indicated unreacted HN_3 and $Ga(CH_3)_3$ as well as sharp features at 3018 and 1306 cm^{-1} attributed to the CH_4 product. In addition to the CH_4 features, new IR bands distinct from those of the reagents were observed at 2118, 2080, and 1251 cm^{-1}. Figure 1 shows a spectrum of the reaction cell after

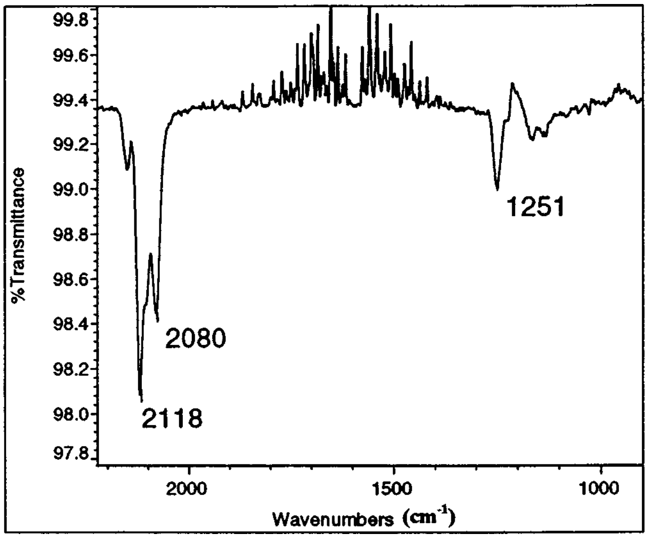

FIG. 1. IR absorption spectrum of the thin film residue left by reaction of 3.25 Torr of $Ga(CH_3)_3$ with 68 Torr of an HN_3/He mixture (10% HN_3) at 300 K.

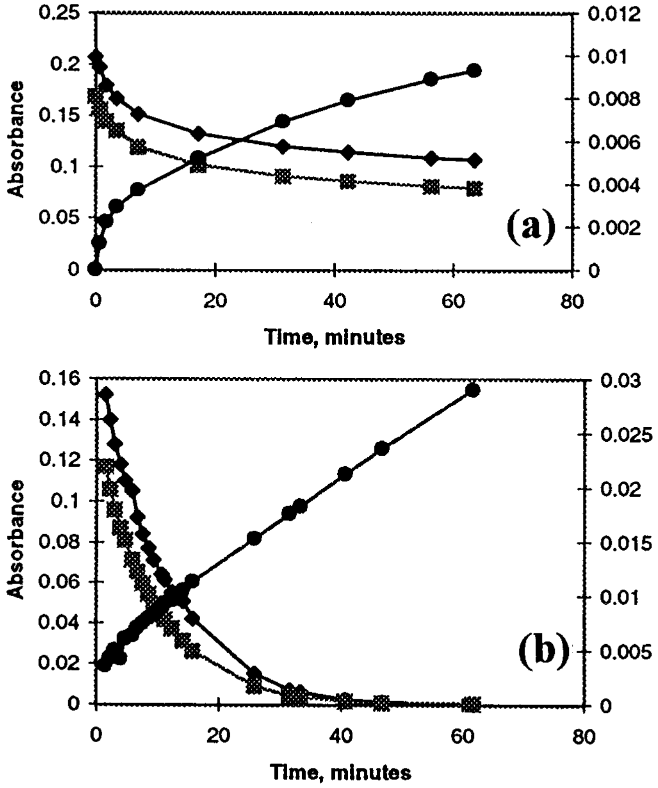

FIG. 2. (a) Time dependence of IR absorbance in a mixture of $Ga(CH_3)_3$ (4.0 Torr) with HN_3/He (120 Torr, 10% HN_3) at 300 K. (b) Time dependence of IR absorbance in a mixture of $Ga(CH_3)_3$ with HN_3/He as in (a), but with UV radiation from a low pressure Hg lamp. (◆) 2156 cm^{-1} absorption in HN_3, (■) 1164 cm^{-1} absorption in HN_3, (●) 3018 cm^{-1} absorption in CH_4.

gaseous species [i.e., CH_4 and unreacted HN_3 and $Ga(CH_3)_3$] were pumped away, hence indicating species left behind as a film residue. The 2118 and 2080 cm^{-1} features remain, as does the weaker feature at 1251 cm^{-1}. The strong 2118 cm^{-1} feature is assigned to molecular N_2 complexed to Ga, by analogy with the frequency of complexed N_2 observed in AlN films.[6,8] The 2080 and 1251 cm^{-1} peaks are assigned to azide substituted gallium. This assignment is supported by the frequencies of analogous features observed in $B(N_3)_3$ and $Al(N_3)_3$ in our earlier work.[5,6] Further, an *ab initio* calculation of the structure and frequencies of $Ga(N_3)_3$ was performed at the MP2/LANL2DZ level of theory.[9] The results of these calculations indicated that this molecule should have intense IR active vibrational modes at 2065 and 1222 cm^{-1}, in very good agreement with the experimental result.

Similar experiments were performed with the reaction mixture [3.0 Torr of $Ga(CH_3)_3$ and 9.0 Torr of HN_3] irradiated continuously by a low pressure Hg lamp. In this case, a dramatic acceleration of the rate of the reaction was observed as shown in Fig. 2. The figure shows that, without UV radiation, the reaction proceeds slowly and the reagents are only partially consumed after more than an hour of reaction time, as described above. In the presence of UV radiation, though, the reaction proceeds quickly and the reagents are fully consumed. CH_4 is evolved throughout the progress of the reaction. Although $Ga(CH_3)_3$ has a weak absorption in the 250 nm region,[10] irradiation of samples of $Ga(CH_3)_3$ with no HN_3 present produced no evidence of reaction; i.e., the IR spectra revealed no loss of the $Ga(CH_3)_3$ initially present and no evolution of products after extended irradiation.

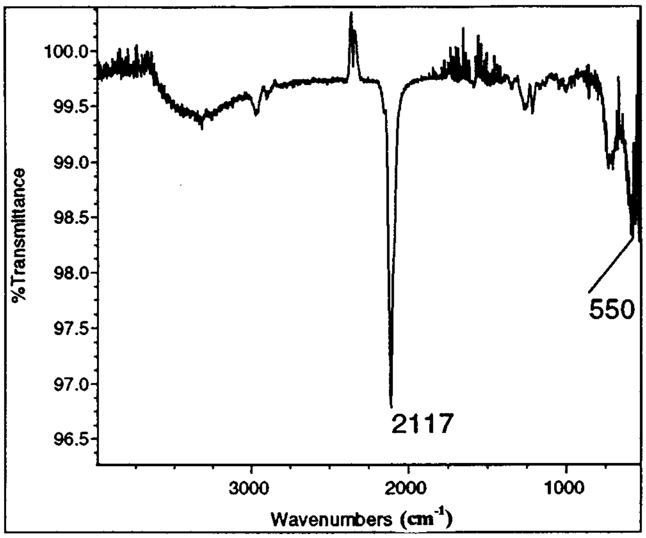

FIG. 3. IR absorption spectrum of the thin film residue left by reaction of 4.0 Torr of $Ga(CH_3)_3$ with 120 Torr of HN_3/He (10% HN_3) in the presence of UV radiation from a low pressure Hg lamp.

Clearly, the UV radiation has either accelerated the thermal reaction, or induced a different mechanism which is much faster. Data such as that shown in Fig. 3 indicates that the latter is the case. The figure shows the IR spectrum of the film residue which remains after the reaction cell has been evacuated, for an experiment in which the UV radiation was used. The intense feature near 2118 cm^{-1} is still present, but the features at 2080 and 1251 cm^{-1} associated with azide substituted gallium are largely absent. There is some evidence of residual $Ga(CH_3)_3$ in the film (features near 2900 and 1215 cm^{-1}). The spectrum also shows a broad, weak absorption centered near 3500 cm^{-1} and two broad bands at low frequency, near 550 and 700 cm^{-1}. Figure 4 shows a typical result of experiments in which film residues deposited under UV radiation were heated at 400 K under an N_2

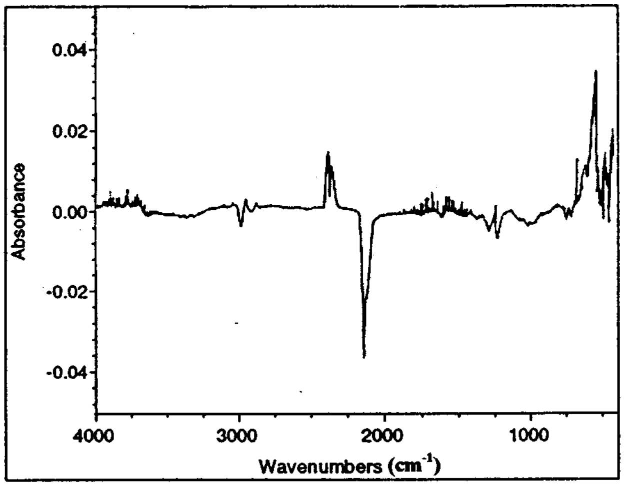

FIG. 4. IR difference spectrum showing changes occurring when a film as in Fig. 3 is heated at 400 K. Negative absorbance corresponds to loss, positive absorbance to growth.

atmosphere. As shown, the absorbance of the complexed N_2 declines sharply, indicating that it is removed by the gentle heating. The major species produced has the sharp absorbance shown at 552 cm^{-1}. This feature is in excellent agreement with the frequency of the E_1 (TO) phonon mode in GaN, and compares well with spectra of GaN films published in the literature.[4]

A number of experiments were performed in which several $HN_3/Ga(CH_3)_3$ mixtures were irradiated in succession over fused silica substrates, with the UV radiation directed through the substrate rather than through the cell wall. This treatment produced very uniform, strongly adherent green films. Measurement of UV/vis absorption spectra indicated an absorption onset near 400 nm, and film thicknesses of 200–400 nm were determined from oscillations in the UV spectra and measurements with a stylus scanner. Analysis with a scanning electron microscopy (SEM)/energy dispersive x-ray analysis (EDAX) indicated very uniform topography (no granularity evident at magnifications up to 100 000x) and the presence of Ga, as expected.

It is clear that the thermal reaction between $Ga(CH_3)_3$ and HN_3 is very slow at room temperature, and occurs only with $Ga(CH_3)_x$ species on the walls of the reaction vessel. The data suggest that this thermal process proceeds in a manner analogous to the reactions of HN_3 with BCl_3 and $Al(CH_3)_3$ to generate azide substituents on the metal, with the release of methane. The large acceleration of the reaction under the influence of UV radiation does not appear to involve the production of azides. The $NH(a^1\Delta)$ produced by photodissociation of HN_3 is isoelectronic to $O(^1D)$ and $CH_2(^1A')$, and is well known[11] to participate in electrophilic insertion reactions as do these species. In the present case, we believe that $NH(a^1\Delta)$ inserts into the Ga–CH_3 bond of the surface-bound $Ga(CH_3)_x$. The transient Ga–NH–CH_3 intermediate thus formed would rapidly eliminate CH_4 to leave surface-bound GaN, as indicated by the IR spectra (Fig. 4). In the gas phase, the $NH(a^1\Delta)$ produced by photodissociation can react rapidly[12] with the parent HN_3 to produce NH_2 and N_2. The NH_2 thus produced can also react with HN_3 to generate NH_3. The broad IR feature centered near 3500 cm^{-1} in the spectrum of the film before warming (Fig. 3) is attributable to the incorporation of NH_3 produced in this manner into the film.

Lin and co-workers[2] have observed enhancement of the rate of deposition of InN produced by CVD at 700 K with HN_3 and $In(C_2H_5)_3$ when the surface is irradiated with the output of a pulsed XeCl laser at 308 nm, and attribute this result to the creation of free N atoms in the surface layer.[13] John and co-workers[14] have reported the photochemically enhanced CVD of GaN on sapphire when mixtures of $Ga(CH_3)_3$ and NH_3 were irradiated with either an ArF laser (193 nm) or a low pressure Xe lamp, at a substrate temperature of 700 K. The mechanism is unknown in this case, but appears to involve fragmentation of both precursors by absorption at wavelengths below 250 nm. Both of these mechanisms appear to be quite different from that found in the present experiments.

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