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GAS PHASE DECOMPOSITION OF AN ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION PRECURSOR TO AlN: $[Al(CH_3)_2NH_2]_3$

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ABSTRACT

A novel technique for probing chemical vapor deposition reaction mechanisms is presented. A conventional hot-wall Pyrex reactor is coupled to a molecular beam apparatus. Preliminary results of the decomposition of an organometallic precursor to AlN, $[Al(CH_3)_2NH_2]_3$, indicate a decomposition temperature between 200 and 270°C. The mass spectrum of the precursor at 100°C provides evidence for the existence of a trimer-dimer equilibrium of the precursor at this temperature.

INTRODUCTION

Organometallic chemical vapor deposition (CVD) has been instrumental in many areas, including: materials science, metallurgy, chemistry and electronics[1]. The experimental studies that have been pursued for many years have centered on properties of the deposited film and optimization of growth conditions[2]. Work has recently begun aimed at understanding the chemical processes and mechanisms which occur during the film growth process in a CVD system[3].

The formation of solid materials by CVD involves a wide range of chemical processes, taking place in several regions of the CVD reactor. If the process requires mixing two or more reactants, association reactions can take place in the gas phase. In all cases, if the gas phase is heated prior to encountering the surface on which growth is to take place, gas phase pyrolysis or reactions on the heated wall surface may occur. There will certainly be surface reactions on the growth surface, and there may be further gas phase or surface reactions among the primary gas phase products in the region beyond the growth surface.

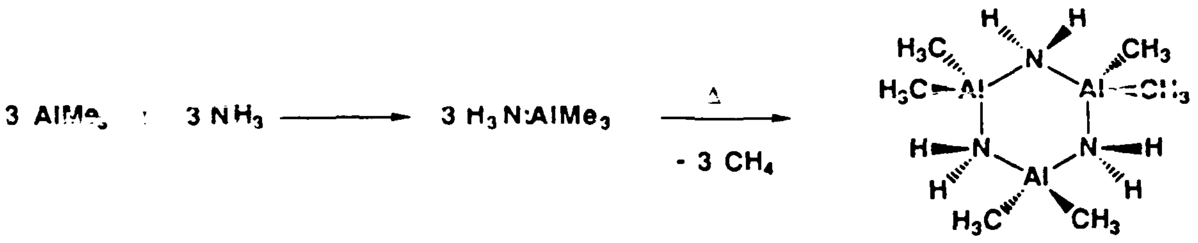
In order to characterize completely the chemistry of the CVD process it is necessary to set up systems in which each of these processes can be studied independently, so that their impact on the overall deposition process may be assessed. We have begun a program of study aimed at this complete characterization process for the case of the deposition of refractory materials such as SiC, AlN and Si_3N_4, from organometallic precursors. In each case the precursor has been synthesized to contain both of the elements to appear in the final product. We are thus dealing with a single precursor system, and the question of gas phase association reactions does not arise. All of the other reaction processes listed above, however, must be accounted for.

We are at present pursuing two lines of approach. In the one case, we have developed a system which involves impinging the precursor on the desired growth surface in an ultrahigh vacuum system, which excludes gas phase reactions. A variety of surface science techniques is used to characterize both the chemistry of the growing film and the gas phase reaction products. This system separates the reaction process at the growth surface from the other gas phase or wall surface reactions.

The second system under study is essentially a hot-wall CVD reactor, with a gas inlet system, coupled to a differentially pumped mass spectrometer. A description of the apparatus is included in the experimental section. This system is being used to study gas phase pyrolysis reactions and reactions on the surface of the hot wall of the reactor; that is, those processes occurring prior to the point at which the precursor flow encounters the growth surface. In this paper we report the initial results obtained using the AlN precursor: $[Al(CH_3)_2NH_2]_3$.

AlN has several properties which make it an attractive candidate for materials applications. It is highly refractory and chemically resistant. It has a large band gap (6.2eV) and a high thermal conductivity (3.2W/cmK). Its thermal expansion coefficient is closely matched to Si, and it is a piezoelectric material. These properties make it an important material for Si-based integrated circuits, optoelectronic devices and surface acoustic wave devices[4].

The organometallic precursor to AlN is prepared according to the following scheme, which has previously been reported by Interrante and coworkers[5]:



The compound exists as a cyclic trimeric species in the solid state[5] and has a vapor pressure of approximately one torr at 70°C. This relatively high vapor pressure makes it a good candidate for use as a CVD precursor. In fact, stoichiometric AlN thin films on Si have been achieved with this precursor using a hot wall reactor at temperatures between 600 and 800°C[6]. An Auger depth profile of these films reveals a one-to-one ratio of aluminum to nitrogen and an oxygen concentration of less than five percent[6].

EXPERIMENTAL

The apparatus built in this study is shown schematically in Figure 1. It consists, in short, of the inlet half of a hot-wall CVD reactor interfaced through a sampling system to a quadrupole mass spectrometer. The precursor is contained in a heated stainless steel bubbler.

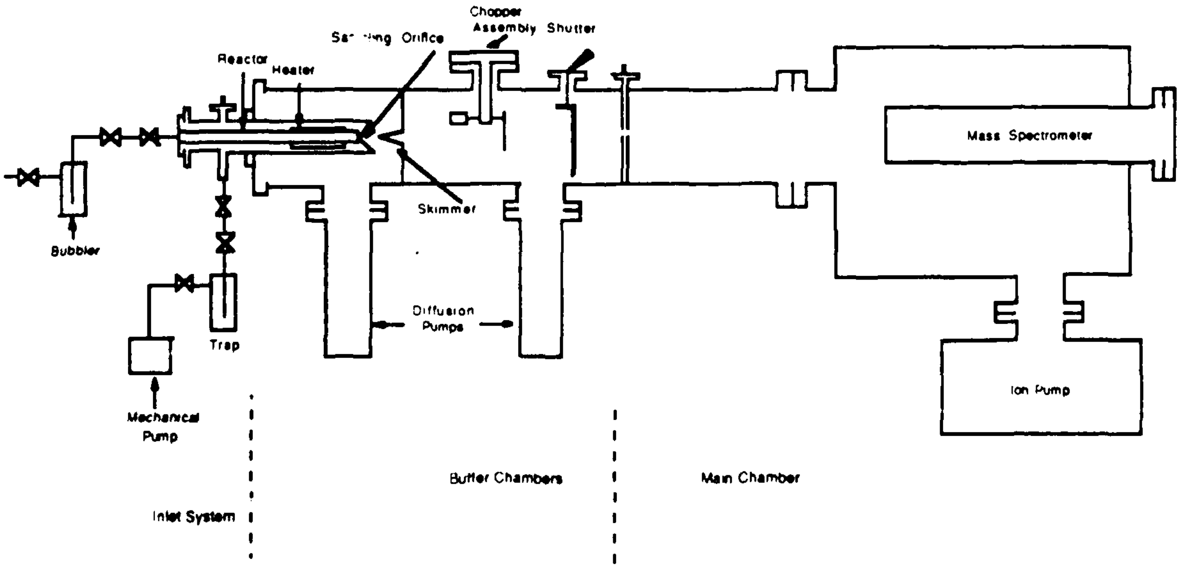


Figure 1. Schematic of the CVD reactor coupled to a differentially pumped mass spectrometer

The precursor can be used either neat or entrained in a carrier gas. In the present study no carrier gas was used. In either case, the precursor flows through a heated inlet system, through the Pyrex reactor tube, and is then pumped away The flow rate through the reactor tube is maintained sufficiently high to insure that the precursor flow makes a single pass through the heated Pyrex reactor tube before being removed by the pumping system. At the end of the Pyrex tube is a sampling orifice, (0.001" in diameter), which is located in a line of sight to the ion source of a quadrupole mass spectrometer. Between the orifice and the mass spectrometer are two stages of differential pumping, labelled as buffer stages in the figure. One stage contains a conical skimmer, (0.020" in diameter) which samples the flow from the orifice. The second stage contains a mechanical chopper assembly and a shutter, both of which are used to discriminate the sample flow from background gas in the mass spectrometer chamber. This setup provides a useable signal at the mass spectrometer, which is maintained at a background pressure in the 10^{-8} torr range, if the reactor pressure is in the torr or above range. The location of the sampling orifice is such that it "sees" the same gas phase species that a substrate would "see" if it were placed in the same location, allowing characterization of the processes taking place in the precursor flow prior to encountering a growth surface. The results reported in this study were obtained with both the bubbler and the inlet system at a temperature of approximately 100°C.

RESULTS AND DISCUSSION

The mass spectrum of the precursor obtained at a reactor temperature of 100°C is shown in Figure 2. This spectrum differs from that obtained by directly introducing the precursor into the ion source of an analytical mass spectrometer by means of a direct inlet probe heated to 40°C. The latter spectrum shows a peak at mass 115(100%) to be the most abundant peak, followed by a peak at mass 204(70%), which corresponds to the parent peak minus a methyl group. A very small parent peak at mass 219(1.4%) is also present. As shown in figure 2, no peaks corresponding to masses larger than 145 were observed with the inlet system and reactor at 100°C; other peaks occur at masses 57, 58, 86, 87, 98, 100, 115, and 131. Table I provides a list of some of the possible assignments to these peaks. Particular attention should be paid to the assignment of the mass 145 peak. This peak may correspond to a dimeric form of the precursor which has lost one H atom. Extensive temperature dependent NMR data have

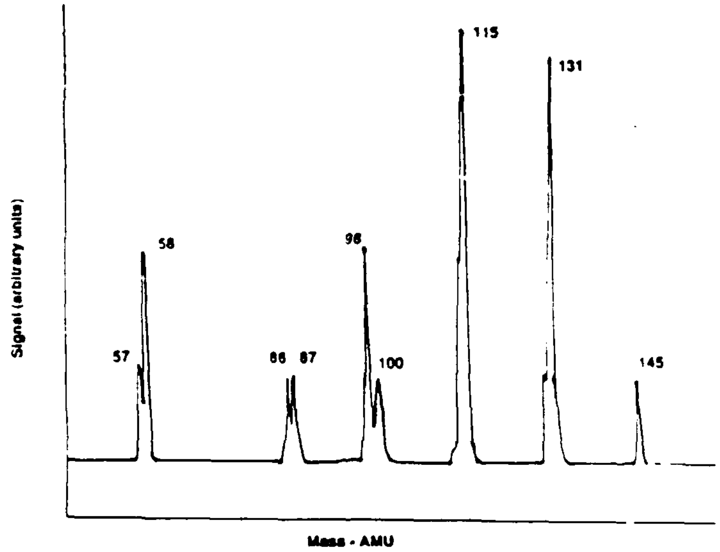


Figure 2. Mass spectrum of the precursor at 100°C

been obtained which indicate the presence of a trimer-dimer equilibrium in solution at elevated temperatures, with a positive ΔH for the formation of the dimer from the trimer[7]. Hence, it would not be unreasonable to speculate that the cracking pattern in Figure 2 is that of a trimer-dimer equilibrium which is shifted essentially completely toward the dimer as a result of maintaining the precursor at 100°C.

Table I. Possible mass peak assignments

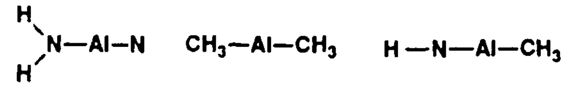
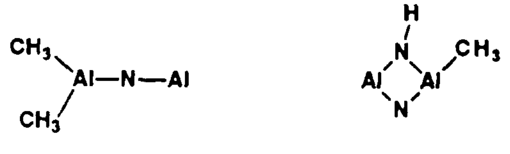
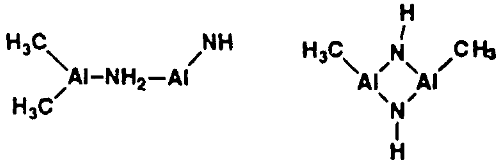
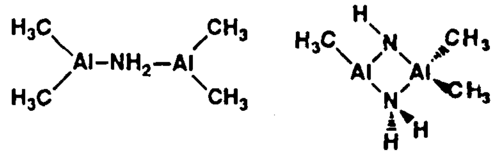
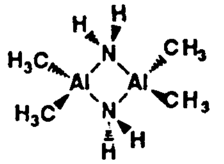
Mass	
57	
98	
115	
131	
146	

Figure 3 is the temperature profile of the mass 115 peak obtained by increasing the temperature of the reactor from 100°C to 400°C over a period of approximately two hours.

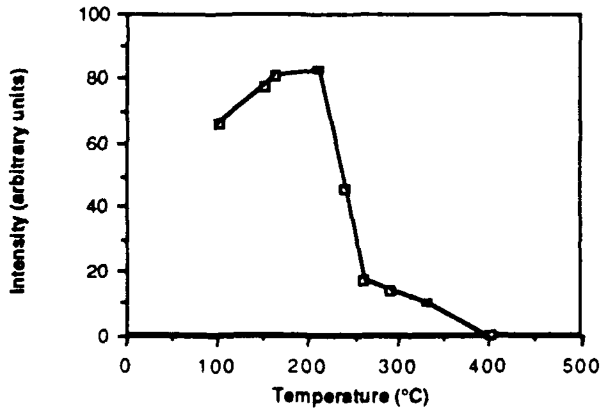


Figure 3. Temperature profile of mass 115 peak

Decomposition of the precursor occurs between the temperatures 200 and 270°C; by 400°C the mass 115 peak completely disappears. The mass 57 and 131 peaks also track this temperature profile. The implication of this is that all three species, mass 57, 115 and 131, are derived from the same species in the mass spectrometer ion source. Given the above information it is possible to offer Schemes 1 and 2 in Figure 4 as mechanistic speculations for the decomposition of the precursor as it flows through the heated Pyrex tube. First, the precursor may exist in rapid trimer-dimer equilibrium. Alternatively, the precursor may already begin to decompose at 100°C by releasing methane and generating a dimeric species as well as a species of mass 57, which is also present in our spectrum. This mechanism is postulated because previous results of Interrante and coworkers[6] reveal methane as a by-product of the CVD process. At the present time a high background signal at low mass numbers prevents us from identifying whether or not methane is one of the decomposition products. Scheme 2 depicts a decomposition of the dimeric species to AlN by way of successive methane elimination. It is interesting that the intermediate species in this pathway have masses which correspond to those observed in our spectra at various temperatures. (Some proposed species may have masses which differ by one mass unit from those observed as a result of proton transfer reactions occurring after electron impact). Alternatively, the peaks corresponding to these masses in our spectra may result from the dimer by fragmentation of the corresponding

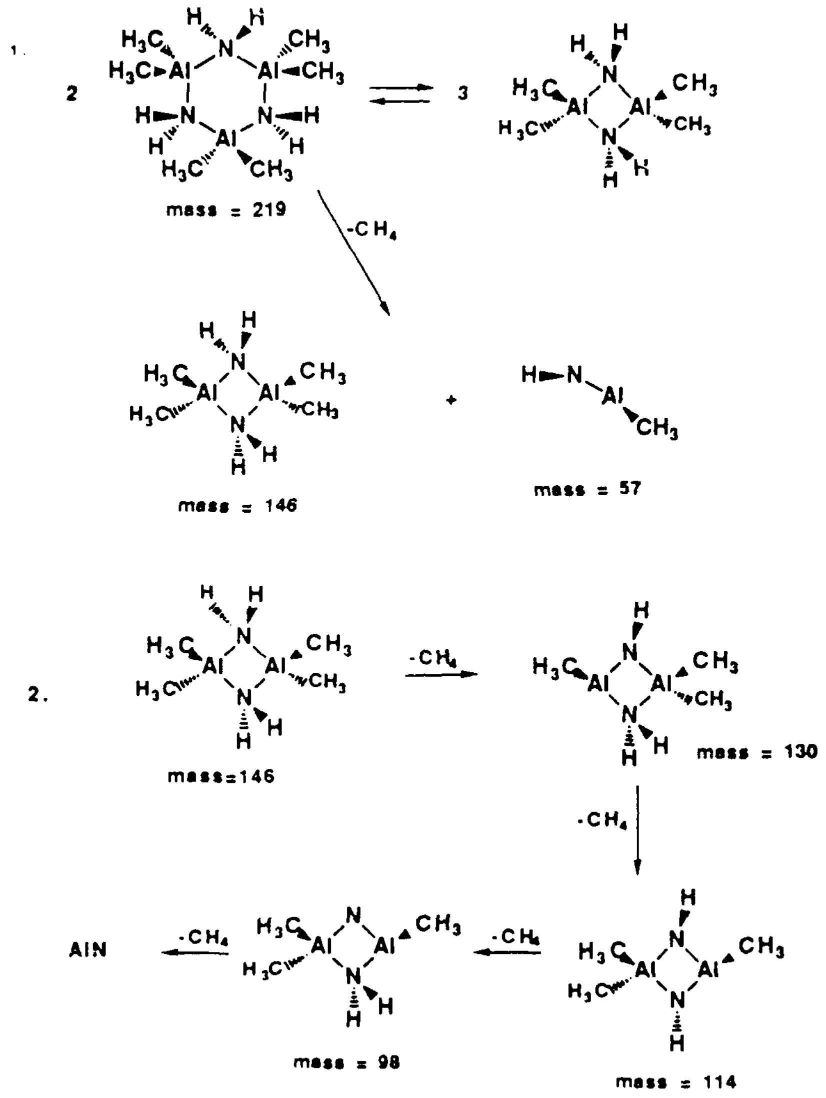


Figure 4. Mechanistic speculation relating to mass spectral cracking pattern

molecular ion in the mass spectrometer. Efforts to distinguish these and other possible decomposition pathways are currently in progress.

CONCLUSION

It has been demonstrated that the coupling of a CVD reactor to a molecular beam apparatus provides a novel technique with which to elucidate CVD mechanisms. Current research efforts are being directed toward the detailed study of the temperature dependence of the trimer-dimer equilibrium and the role of these species in the CVD process. Isotopically substituted analogues of the precursor have been prepared to help determine the structure of the species which give rise to the peaks observed in our mass spectra.

Also, the question still remains as to whether any or all of the species observed during the decomposition are a result of purely gas phase pyrolysis or a result of gas interactions with the Pyrex reactor. In order to address this issue, it is planned to repeat the above experiments with the addition of a flow of inert carrier gas through the reactor. Provided that laminar flow conditions are maintained, the inert gas will inhibit reaction of the precursor with the surface of the reactor walls.

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