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13. ABSTRACT (Maximum 200 words)

Cyclic molecular systems of the type, $[A(XX')B(YY')]_n$ (where A, B = Al, N or Si, C; X, X', Y, Y' = H, CH3, etc. and n = 2 and 3), were studied as potential single-source precursors for the CVD of AlN and SiC films. These compounds provide the required elements for the product film already covalently bound to one another in a single, volatile molecular source and, in the case of the SiC precursors (where n = 2), they contain built-in ring-strain energy to lower the decomposition onset temperature. Efforts have included the study of the $[(CH_3)_2AlNH_2]_3$ --> AlN CVD system by mass-spectrometric/time-of-flight measurements and the investigation of substituted disilacyclobutanes as single-source SiC precursors. The mass-spec/TOF studies have indicated that a slow decomposition of the $[(CH_3)_2AlNH_2]_3$ (I) precursor to produce methane and a series of higher oligomeric products occurs during its vaporization at 75-100 $^\circ$C. These oligomeric species are believed to be intermediates formed in the gas-phase thermal decomposition of I to AlN. This precursor was used to deposit high quality AlN films up to 2 μm thick on Si and sapphire substrates in a LPCVD apparatus and is being tested for use in the deposition of AlN interface layers in Al_2O_3-reinforced metal matrix composites. Disilacyclobutane, $[SiH_2CH_2]_2$, was found to yield stoichiometric, crack-free, adherent, polycrystalline SiC films on Si (100) and Si (111) surfaces by LPCVD at temperatures as low as 690 $^\circ$C. Comparative studies of this and the related disilacyclobutane derivatives, 1,3-dimethyl-1,3-disilacyclobutane (II) and 1,3-dimethyl-3-methylsilamethylene-1,3-disilacyclobutane (III) carried out in a hot-wall, cold-stage LPCVD reactor revealed that the decomposition/SiC-deposition temperature decreases with increasing H-substitution on Si, with the parent DSCB having the lowest decomposition temperature.

14. SUBJECT TERMS
chemical vapor deposition (CVD); AlN; SiC; organometallic precursor

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SYNTHESIS AND STUDIES OF ORGANOMETALLIC PRECURSORS

FOR CVD OF THIN FILM ELECTRONIC MATERIALS

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30 September 1994

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OBJECTIVE

The chief objective of this research effort was to explore certain design strategies for the development of suitable single-source precursors for the CVD of compound wide band gap semiconductors and insulators of potential interest for applications in electronics. Taking AlN, SiC and Si_3N_4 as the three target inorganic product films, various volatile compounds containing Al (or Si) and N (or C) were chosen for an examination of the effects of precursor structure and substituents on the composition and microstructure of the product films. For Si_3N_4 and AlN, one particular precursor ($Si(NHEt)_4$ for Si_3N_4 and $[Me_2AlNH_2]_3$ for AlN) was selected in each case for CVD and thermal decomposition studies, and with $[Me_2AlNH_2]_3$, for a detailed study of the gas phase species by molecular beam mass spectrometry. The use of $Si(NHEt)_4$ for SiN_4 CVD was prompted by the expectation that the Et substituents on the N might provide an opportunity for loss of the organic substituents on N via a β-hydrogen-type elimination process. For SiC, the availability of a series of 4-membered $(SiC)_2$ ring compounds with H on C and various substituents (H, Me and CH_2SiH_2Me) on Si, allowed the study of both the effect of ring strain and substituent-related mechanistic differences on the decomposition temperature and composition/microstructure of the product films. The availability of prior gas phase decomposition studies on some of the latter compounds ($[SiR_2CH_2]_2$, R = H and Me, gave further insight into the expected mechanistic differences. In the case of AlN, the cyclic, dimethylaluminum amide, $[Me_2AlNH_2]_3$ again provided a volatile molecular source containing the basic elements needed in the product film along with a favorable pathway for eliminating the Al and N substituents as a stable gaseous byproduct (CH_4).

APPROACH

In the case of $Si(NEt_2)_4$, films were deposited in a hot-wall CVD reactor on Si substrates at 800 °C and analyzed ex-situ by XRD and Auger spectroscopy. A study of the solid products of decomposition by solid state NMR, IR and XRD at various temperatures was also independently conducted on both $Si(NMe_2)_4$ and $Si(NEt_2)_4$ to determine the evolution of composition and microstructure with temperature.

The $[Me_2AlNH_2]_3$ and the three disilacyclo-butanes, $[SiRR'CH_2]_2$, R, R' = H; R = H, R' = Me; and $[Si(H)MeCH_2Si(Me)CH_2SiH_2Me]$, were examined in a cold-wall, hot-stage, stainless steel LPCVD reactor equipped with a turbomolecular pumping system and a quadrupole mass spectrometer. Films were deposited on Si substrates at various temperatures and then analyzed by ex-situ XRD, Auger spectroscopy and SEM to determine the composition and microstructure. In-situ, mass spectrometric detection of gaseous byproducts were used to determine the decomposition onset temperatures and to determine the distribution of permanent gaseous products as a function of temperature. More detailed studies of the gas phase species by using mass-spectrometric/time-of-flight methods, and the surface chemistry by molecular beam scattering, were conducted in selected cases to elucidate the reaction pathways.

With the help of Dr. John Hudson in the Rensselaer Materials Engineering Department at Rensselaer, a molecular effusion source that simulates a hot-wall CVD reactor containing the $[Me_2AlNH_2]_3$ precursor was set up. The molecular beam of precursor vapor emanating from this reactor is modulated by a mechanical chopper to provide a pulse of molecular species that is detected, after a certain distance of travel, by a quadupole mass spectrometer. The measured time-of-flight, coupled with the observed cracking pattern, provides a reasonably unambiguous identification of the molecular masses of the species present in the gas phase along with an indication of their possible structure.

BACKGROUND

Materials such as SiC and AlN have enjoyed continued interest and attention over the past several decades for a wide range of applications in electronics and as structural materials [1,2]. In the case of SiC, this interest has been enhanced recently by the successful fabrication, by CVD, of SiC electronic and optoelectronic devices with excellent performance characteristics as well as by the use of chemical vapor infiltration (CVI) to prepare SiC-matrix composites with high strength and thermal/oxidative stability characteristics [1]. Similarly, for AlN, its high thermal conductivity coupled with the high band gap and close expansion match with Si has engendered much current interest in this material for IC substrates. Moreover, its excellent oxidative/thermal stability as well as its piezoelectric and other useful electrical and mechanical properties have made it increasingly attractive as thin film material for a wide range of electronic and structural applications [2].

These applications for SiC and AlN could all benefit from improved, single-source, LPCVD precursors which would lower the temperature required to obtain the desired film properties, or just simplify the CVD process. For example, in the case of SiC, Mixtures of silane, or chlorosilanes, and hydrocarbons, or CH_3SiCl_3 are typically employed for CVD applications; however, the use of hydrogen as a carrier gas is generally required in these applications and substrate temperatures in excess of 1000 °C are needed to control the film composition and crystallinity [3]. Moreover, the film composition and properties are strongly dependent on the deposition conditions and the local concentrations of the reactant species, which is difficult to control under many CVD situations, such as, for example, in the CVI of SiC matrices or composites. The situation for AlN is even more problematic, where the typical CVD sources for Al and N, such as AlX_3 or Me_3Al and NH_3 either undergo pre-reaction in the gas phase, thereby requiring unusual precautions to avoid premixing during CVD, and/or are so involatile that the deposition rates and reactor design considerations are unduly compromised [4]. Here again, control of the film composition and microstructure in these CVD processes is problematic and relatively high system pressures with hydrogen as a carrier gas are generally required.

In our past research under ONR support, we demonstrated that certain cyclic organometallic compounds which contain Al and N or Si and C as the ring constituents can be used as convenient single-source LPCVD precursors for AlN and SiC. We showed, in particular, that the compound, $[(CH_3)_2AlNH_2]_3$, has sufficient volatility for LPCVD application and that it yields pure, polycrystalline AlN films at substantially lower temperatures than has been reported previously by using separate precursors for Al and N [5]. A cyclic organosilicon compound,

$[Si(H)MeCH_2Si(Me)CH_2SiH_2Me]$, was also found to yield a C-rich SiC film at a considerably lower temperature than had previously been demonstrated for related non-cyclic carbosilanes [6]. The current study was directed, in part, at examining further the use of such cyclic organometallic precursors for the CVD of AlN and SiC, and in determining, for the SiC precursors, the effects of changes in the ring substituents on the decomposition temperature as well as the composition and microstructure of the product films.

SCIENTIFIC CONCLUSIONS

Prior studies of $Si(NMe_2)_4$ as a Si_3N_4 CVD source had resulted in SiC_xN_y films that contained more carbon than nitrogen. Our efforts to use $Si(NHEt)_4$ as a single-source Si_3N_4 CVD precursor also yielded amorphous SiC_xN_y films which contained substantial amounts of carbon; however, the proportion of retained nitrogen in these films was higher than that obtained by using $Si(NMe_2)_4$ and the predominant permanent gaseous product detected was ethylene, as would be expected if a β-elimination of H from the N-Et groups was indeed occuring. Initial attempts were made to carry out depositions by using this precursor in combination with gaseous NH_3; however, these efforts were abandoned when the successful deposition of Si_3N_4 by this same route was reported by Hoffman and Gordon [7]. Further studies of the thermal decomposition of the related $Si(NHMe)_4$ and $Si(NHEt)_4$ compounds were carried out by heating bulk samples to various temperatures under N_2 and examining the solid products by solid state NMR, XRD and IR methods [P4]. The key findings were that the initial SiN_4 environment of the Si atoms in these compounds was retained to at least 800 °C, at which temperature the remaining organic (Et or Me) substituents had been converted largely to free carbon. This SiN_4 environment could be further preserved on heating to 1600 °C if the heating were carried out under N_2; however, in an inert atmosphere (Ar or vacuum) the Si-bound N is lost (presumably as N_2), yielding SiC as the main Si-containing phase.

The results of the study of the AlN precursor include the identification of a significant rate of decomposition of the precursor under the conditions employed for its vaporization (i.e., 75-100 °C at ca. 1-10 Torr) producing methane (or CH_3D in the case of the N-deuterated precursor) and a series of higher oligomeric products that have lost one or more molecules of methane, including a pentamer of the composition, $(CH_3)_9Al_5N_5D_9$. Moreover, the trimeric form of the amide precursor is apparently in equilibrium in the gas phase, as it is known to be in solution at these temperatures [8], with the corresponding dimeric form, $[Me_2AlNH_2]_2$. These results suggest that the gas phase, and probably also the surface, chemistry of this precursor when used as a LPCVD source are quite complex, with the nature of the species present, and thereby the product film, highly dependent on the precursor partial pressure and the system temperature [P1, P6, P8, P11]. This conclusion is supported by our studies of this system as an LPCVD source in both hot- and cold-wall CVD reactors, where the most uniform, dense, highly crystalline films are obtained under conditions of relatively low precursor partial pressures. Despite these shortcomings, under appropriate conditions, high quality, polycrystalline AlN films can be obtained by using this precursor at substantially lower temperatures than has been demonstrated with other single source or multi-source precursors.

Our studies of the disilacyclobutane derivatives, 1,3-disilacyclobutane (I), 1,3-dimethyl-1,3-disilacyclobutane (II) and 1,3-dimethyl-3-methylsilamethylene-1,3-disilacyclobutane (III) revealed that the decomposition/SiC-deposition temperature decreases with increasing H-substitution on Si, with the parent DSCB (I) having the lowest decomposition temperature. Ex-situ film characterization by Auger and XRD indicated that the film composition and crystallinity varies with the deposition temperature, and the choice of the precursor, with DSCB giving the purest, most crystalline, SiC films at the lowest temperature [P2, P5, P8, P9].

Molecular beam studies of the surface reactions of precursors II and III on Si, conducted by Dr. J. Hudson, revealed a variety of primary desorption products which presumably either go on to react with the surface in a CVD reactor or interact with the walls of the reactor and/or other gas molecules to produce the observed longer-lived decomposition products observed in the LPCVD reactor. The species identified as surface desorption products in these cases are

consistent with a previously suggested decomposition mechanism for disilacyclobutanes which involves a 1, 2, Si-to-C, hydrogen-shift accompanied by opening of the strained disilacyclobutane ring to form silylene (RR'Si:) species [P12].

A key result of this study has been the identification of the parent disilacyclobutane, $[SiH_2CH_2]_2$, as an excellent thermal CVD source for high quality, polycrystalline SiC films [P5]. This initial observation in the LPCVD reactor has recently been confirmed by further, more detailed, studies which have focused on the examination of the gas phase byproducts and the film composition as a function of substrate temperature, precursor partial pressure, and in hot- *vs* cold-wall CVD apparatus. Crack-free, adherent, polycrystalline, SiC films have been produced on Si (100) and Si (111) surfaces by using this precursor at temperatures as low as 650 ºC.

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P1. C.C Amato, J.B. Hudson, and L.V. Interrante, "Gas Phase Decomposition Chemistry of an Organometallic Precursor to AlN Prior to Deposition", Chemical Perspectives of Microelectronic Materials II, Mats. Res. Soc. Sympos. Proc., 204, 135 (1991).

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P4. D.M. Narsavage, L.V. Interrante, P.S. Marchetti, and G. Maciel, "Condensation Polymerization of Tetrakis(ethylamine)silane and its Thermal Decomposition to Si_3N_4/SiC Ceramics", Chem. Mater., 3, 721 (1991).

P5. D. Larkin and L.V. Interrante, "Chemical Vapor Deposition of Silicon Carbide From 1,3-Disilacyclobutane" Chem. Mater. 4, 22 (1992).

P6. C. Amato, J.B. Hudson, and L.V. Interrante, "Identification of the Gas Phase Products Which Occur During the Deposition of AlN Using the Organometallic Precursor: $[(CH_3)_2AlNH_2]_3$", Applied Surface Science, 54, 18 (1992).

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P8. L.V. Interrante, D. J. Larkin and C. Amato, "CVD of AlN and SiC Using Cyclic Organometallic Precursors", MRS Symp. Proc., 250, 283-290 (1992).

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P12. B. Han, J.B. Hudson, and L.V. Interrante, "Surface Decomposition Kinetics of Organosilane Precursors to Silicon Carbide", Mats. Res. Soc. Sympos. Proc., 282, 457-462 (1993).

P13. F. Sauls and L.V. Interrante, "Coordination Compounds of Aluminum as Precursors to Aluminum Nitride", Coord. Chem. Revs., 128, 193-207 (1993).

Book Edited

"Chemical Prespectives of Microelectronic Materials", Mat. Res. Soc. Symp. Proc., Vol. 204, K. Jensen, L. DuBois, and M. Gros, co-editors, published by the Materials Research Society, 584 pages (1991).

HIGHLIGHTS OF THREE PUBLICATIONS RESULTING FROM THE RESEARCH PROGRAM

1. D. Larkin and L.V. Interrante, "Chemical Vapor Deposition of Silicon Carbide From 1,3-Disilacyclobutane" Chem. Mater. 4, 22 (1992).

This paper reported the identification of a new single-source precursor for LPCVD of stoichiometric SiC films, 1,3-disilacyclobutane (DSCB). This precursor has a 1:1 Si:C ratio with H as the substituents on both Si and C. It also has a strained 4-membered (SiC)$_2$ ring structure which should facilitate decomposition at a relatively low substrate temperature. In fact, decomposition of the precursor, and deposition of near stoichiometric SiC, was detected as low as 680 °C and films deposited above ca. 900 °C were stoichiometric, polycrystalline β-SiC. These temperatures are considerably lower than those which have been used previously to deposit crystalline SiC films and the control of stoichiometry at the desired 1:1 Si:C ratio is also considerably improved relative to these earlier studies. These results suggest that DSCB precursor is an excellent candidate for epi-growth of SiC films on single-crystal SiC or appropriately preconditioned Si substrates.

2. F. Sauls and L.V. Interrante, "Coordination Compounds of Aluminum as Precursors to Aluminum Nitride", Coord. Chem. Revs., 128, 193-207 (1993).

This paper reviews our past and current studies of organoaluminum amides as precursors to AlN. The structures and chemistry of both the cyclic dialkyaluminum amides that result from the reaction of R$_3$Al and NH$_3$ and the oligomeric/polymeric products that are obtained by

combining R_3Al and ethylenediamine are described along with our efforts to use these compounds as precursors for AlN powder and AlN films.

3. D.M. Narsavage, L.V. Interrante, P.S. Marchetti, and G. Maciel, "Condensation Polymerization of Tetrakis(ethylamine)silane and its Thermal Decomposition to Si_3N_4/SiC Ceramics", Chem. Mater., 3, 721 (1991).

$Si(NHEt)_4$ undergoes a thermally-induced condensation polymerization which eliminates ethyl- and diethyl-amine and produces a highly crosslinked polymer that contains Si in a SiN_4 environment, linked by -N(Et)- bridges and containing terminal -NHEt groups. This study employs solid state NMR and other methods to characterize the structure of the starting polymer as well as the thermal evolution of this polymer to ceramic products on pyrolysis. A key finding was that the intial SiN_4 environment of the starting polymer is preserved during the thermal decomposition of the organic (Et) groups, yielding an amorphous structure that contains a silicon nitride-like SiN_4 environment along with free carbon. The thermodynamically favored products of SiC and N_2 are only obtained after further heating to 1600 °C in Ar or vacuum, whereas even 1 atm environment of N_2 is sufficient to supress loss of the N_2 from the SiN_4 groups, yielding Si_3N_4 as the predominant Si phase. This system provides an excellent demonstration of the ability to control the outcome of precursor pyrolysis through subtle changes in the pyrolysis conditions as well as the importance of the initial precursor structure in determining the composition and microstructure of the final ceramic phase.

PRESENTATIONS

L.V. Interrante, "The Design and Synthesis of Organometallic Precursors to Refractory Ceramic Materials", Seminar, University of Kentucky, April 2, 1991.

L.V. Interrante, "The Design and Synthesis of Organometallic Precursors to Refractory Ceramic Materials", Seminar, General Electric CRD, Schenectady, NY, May 1, 1991.

L.V. Interrante, "The Design and Synthesis of Organometallic Precursors to Refractory Ceramic Materials", Seminar, New England Organometallic Workshop, Yale University, May 11, 1991.

L.V. Interrante, "Molecular Routes to Solid State Inorganic Materials: Organoaluminum Compounds as Precursors to Aluminum Nitride", Seminar, Queen Mary College, London, England, June 10, 1991.

L.V. Interrante, "Molecular Routes to Solid State Inorganic Materials: Preparation of Aluminum Nitride and AlN/SiC Solid Solutions Using Organometallic Precursors", Seminar, Institute of Materials, University of Nantes, June 14, 1991.

L.V. Interrante, "Synthesis of Novel Inorganic Materials by Pyrolysis of Organometallic Precursors", Seminar, Tokyo Institute of Technology, Tokyo, Japan, July 12, 1991.

L.V. Interrante, "CVD of SiC and AlN Using Organometallic Precursors", invited paper, Meeting on Electronic Ceramics, Shonan Institute of Technology, Fujisawa, Japan, July 20, 1991.

L.V. Interrante, "Disilacyclobutanes as Single-Source Precursors for LPCVD of SiC", invited paper, Symposium on Molecular Routes to Materials, NY City ACS Meeting, August 25, 1991.

L.V. Interrante, "CVD of SiC Using Disilacyclobutanes", seminar, AT&T Bell Labs., Sept. 9, 1991.

L.V. Interrante, "CVD of SiC Using Disilacyclobutanes", seminar, ATM Inc., Danbury, CT, Oct. 18, 1991.

L.V. Interrante, "CVD of SiC and AlN Using Organometallic Precursors", invited paper, Symposium R, CVD of Refractory Metals and Ceramics, MRS Meeting, Boston, MA, December 6, 1991.

L.V. Interrante, "The Design and Synthesis of Organometallic Precursors to Refractory Ceramic Materials", Seminar, Dow Corning Research Lab., Midland, MI, March 2, 1992.

L.V. Interrante, "Chemical Vapor Deposition of Thin Films Using Cyclic Organometallic Precursors", Materials Science Program Seminar, University of North Carolina, Chapel Hill, March 20, 1992.

L.V. Interrante, "The Design and Synthesis of Organometallic Precursors to Refractory Ceramic Materials", Seminar, Chem. Dept., Univ. of Oregon, Eugene, April 3, 1992.

L.V. Interrante, "Coordination Compounds of Aluminum as Precursors to Aluminum Nitride", J.C. Bailar Memorial Symposium, Inorganic Division, ACS, ACS National Meeting, San Francisco, April 8, 1992.

L.V. Interrante, "Fundamentals and Chemistry of CVD Processing", Short Course on CVD, Rensselaer Polytechnic Institute, July 1992, 1993 and 1994.

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L.V. Interrante, "CVD of SiC and AlN", Seminar, Plate Glass Research Labs, PPG Industries, November 4, 1992.

L.V. Interrante, "Materials Chemistry", Frontiers in Chemistry Lecturer, Wayne State University, Detroit, MI, March 9, 1993.

L.V. Interrante, "Chemical Vapor Deposition of AlN Using Organoaluminum-Nitrogen Compounds", invited paper, Symposium on Surface Chemistry of Advanced Materials", Division of Colloid and Surface Chemistry, ACS National Meeting, San Diego, CA March 14, 1993.

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L.V. Interrante, "Organometallics and Materials Chemistry" NSF Solid State Chemistry Undergraduate Summer Research Program, Toutorial Presentation, SUNY Binghamton, June 10, 1993.

B. Han, J.B. Hudson, and L.V. Interrante, "Surface Decomposition Kinetics of Organosilane

Precursors to Silicon Carbide", Materials Research Society, Symposium E, "Chemical Perspectives of Microelectronics Materials III", December, 1993.

C. Amato, J.B. Hudson, and L.V. Interrante, "The Decomposition Chemistry of An AlN Precursor Bis-Dimethylaluminum Deutero-amide, $[(CH_3)_2AlND_2]_3$, as Revealed by Time-of-Flight Molecular Beam Mass Spectrometry", Materials Research Society, Symposium E, "Chemical Perspectives of Microelectronics Materials III", December, 1993.

AWARDS (HONORS)

Member, External Advisory Committee, NSF Science and Technology Center for Synthesis, Growth and Analysis of Electronic Materials, University of Texas at Austin. 1991-present

17th Annual Waite Phillip Fishel Lecturer, Vanderbilt University, Nashville, TN, October 12, 1993.

Honorary Member, Materials Research Society of India, elected February 1994.

HIGHLIGHTS OF A PRESENTATION AND AN AWARD (HONOR)

Presentation (and Award):

Frontiers in Chemistry Lecturer, Wayne State University, Detroit, MI, March 9, 1993.

This presentation summarized our work on both MOCVD and polymeric precursors to ceramic materials in the context of the growing interest in materials chemistry worldwide.

Honor:

Member, External Advisory Committee, NSF Science and Technology Center for Synthesis, Growth and Analysis of Electronic Materials. University of Texas at Austin. 1991-present

For the last three years, since its inception in 1991, Dr. Interrante has served on the external advisory committee of this NSF Science and Technology Center. This advisory committee consists of eleven scientists and engineers from industry, academic and governmental laboratories and advises the Center Director, Dr. M. White, and the Dean of Science, UT on the operation of this Center.

TRANSITIONS

Interaction with Dr. David Larkin, NASA Lewis Research Center, Cleveland:

Dr. Larkin, a former Ph.D. student of Dr. Interrante's, has been at NASA Lewis since leaving Rensselaer in 1991 working with Dr. Tony Powell and others on the epi-growth of device quality SiC. He has funded through NASA a small effort in our laboratory to supply the single-source SiC CVD precursor that we developed to him at NASA for use in his epi-growth studies.

Interaction with Drs. John Hudson and William Hillig of the Rensselaer Composite Materials Center:

We have supplied precursor ($[(CH_3)_2AlNH_2]_3$) and process information to these individuals relating to the CVD of AlN for use as an interface coating in alumina fiber-reinforced, metal matrix composites. They have found that this single-source precursor can be used to coat the alumina fiber with a continuous AlN layer that resists attack of the $MoSi_2$ metal matrix and the HCl byroduct gas produced during its fabrication by reactive CVI.