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The principal focus of this Project was the design and synthesis of volatile organometallic precursors for the LPCVD of AlN, SiC, and other materials of interest for applications in electronics. As potential precursors for AlN, and SiC, various cyclic compounds 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 prepared and studied. The pyrolytic decomposition of these compounds were investigated using mass spectrometry and IR spectroscopy and the resultant thin films examined by Auger spectroscopy and SEM/TEM to determine the composition, microstructure, and purity of the phases present. Through the use of selected precursors of this type, high quality, films of stoichiometric AlN and SiC were obtained at temperatures (500 - 800 °C) well below that employed in previous investigations.

Thin films of both AlN and the cuprate superconductors were also prepared by pyrolysis of solution-applied polymeric precursor films. The AlN films were obtained from ethylenediamine:triethylaluminum derivatives and the cuprate superconductors from citric acid/ethyleneglycol mixtures containing the respective metal nitrate salts. The structures and pyrolysis reactions of these polymeric precursors were studied by NMR, FTIR, XRD and other methods.
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A Program in the Chemistry of Electronic Materials
At the Department of Chemistry
Rensselaer Polytechnic Institute

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NEW ORGANOMETALLIC PRECURSORS FOR THE LOW PRESSURE CHEMICAL VAPOR DEPOSITION OF REFRACTORY MATERIALS FOR ELECTRONICS

Prof. L.V. Interrante

SUMMARY

The principal focus of this Project was the design and synthesis of volatile organometallic precursors for the LPCVD of AlN, SiC, and other materials of interest for applications in electronics. As potential precursors for AlN, and SiC, various cyclic compounds of the type, \( [A(XX')B(YY')]_n \) (where \( A, B = Al, N; \) or \( Si, C; \) \( X,X',Y,Y' = H, CH_3 \), etc. and \( n = 2 \) and \( 3 \) ), were prepared and studied. The pyrolytic decomposition of these compounds were investigated using mass spectrometry and IR spectroscopy and the resultant thin films examined by Auger spectroscopy and SEM/TEM to determine the composition, microstructure, and purity of the phases present. Through the use of selected precursors of this type, high quality, films of stoichiometric AlN and SiC were obtained at temperatures (500 - 800 °C) well below that employed in previous investigations.

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BACKGROUND

The present study was begun in 1985 in the context of a multi-investigator program in the chemistry department at Rensselaer that was directed broadly at the application of chemistry to electronics. This program seeded the development of three different research efforts in electronic materials chemistry and made possible the purchase of a TGA/DSC
system which we have used extensively in the course of our precursor synthesis and evaluation efforts.

The program also provided funds for the construction of a cold-wall, hot-stage CVD system in our laboratory which has been used to evaluate new CVD precursors and to prepare thin films of AlN and SiC for examination of electrical and optical properties. This apparatus has recently been upgraded by adding a mass flow controller and quadrupole mass spectrometer, allowing control of precursor flow rates and on-line mass spectral analysis of precursor decomposition products. A more detailed description of this apparatus is included as Appendix A of this report.

RESULTS

A major focus of this program has been the design and synthesis of volatile organometallic precursors for the low pressure chemical vapor deposition of aluminum nitride and silicon carbide for applications in electronics. As potential precursors for these materials, various cyclic compounds of the type, \([A(XX')B(YY')]_n\) (where \(A, B = Al, N\); or \(Si, C\); \(X,X',Y,Y' = H, CH_3, \) etc. and \(n = 2\) and \(3\)), were prepared and studied. In addition, a monomeric silicon tetraamide was examined as potential low pressure CVD precursor to \(Si_3N_4\). The study of these compounds has included the investigation of their pyrolytic decomposition, by analysis of the volatile decomposition products, and also the examination of the product thin films to determine their composition, microstructure, purity and properties.

The cyclic precursor, \([Me_2AlNH_2]_3\), was used to deposit high quality, polycrystalline thin films of AlN on Si and other substrates at considerably lower temperatures than had been required previously to obtain films of this type. Separate studies of this precursor system in solution, by NMR spectroscopy, revealed a rapid equilibrium involving the dimeric and, presumably, the monomeric form of this compound and Generalized Valence Bond calculations were performed that indicated a planar structure and a significant stability for this monomer. Recent mass spectral studies carried out in collaboration with J. Hudson have suggested that this trimer-dimer equilibrium extends also to the gas phase and that the active species in the CVD process may be one of these other forms of the \([Me_2AlNH_2]_3\) precursor. Efforts to study both the gas phase and surface
chemistry of this precursor are continuing.

In the course of this program a new volatile precursor to SiC was also identified and used to prepare thin films of apparently stoichiometric SiC at temperatures as low as 600 °C. This precursor is a volatile, liquid, cyclic carbosilane, \([\text{MeSi(H})\mu(\text{CH}_2)_2\text{Si(Me)CH}_2\text{SiH}_2\text{Me}]\), derived from the Grignard coupling of \(\text{Cl}_2\text{Si(Me)CH}_2\text{Cl}\). It was employed as a single-component precursor for SiC deposition on a Si(100) surface in both a hot-wall, SiO\(_2\) reactor and in Prof. Hudson’s ultrahigh vacuum system. In both cases smooth, dense, adherent SiC films were obtained; however, the microstructure of the deposit was found to depend on the reaction conditions, with a fine-grained amorphous deposit resulting from the hot-wall reactor at 600-800 °C and a polycrystalline deposit from the experiments in the ultrahigh vacuum system. Thermal desorption experiments carried out in Professor Hudson’s laboratory have revealed a two-peak desorption profile which appears to relate to the cis- trans-isomer distribution present in the precursor source. The onset of a chemical process leading to CVD of stoichiometric SiC at ca. 500 °C was also evidenced.

Efforts to deposit \(\text{Si}_3\text{N}_4\) using volatile, single-component precursors centered on the use of silazanes in which the Si is bound only to nitrogen. Initial work with \(\text{Si(NHEt})_4\) gave black films on Si which contained Si, C, and N by Auger analysis. The proportion of N to C was found to depend on the deposition conditions; however, significant amounts of carbon were observed in all cases. Preliminary results suggested that a significant reduction in the carbon content could be achieved by the addition of ammonia to the gas stream containing this precursor. Subsequently, this conclusion was verified in an independent study by Gordon and Hoffman who used this precursor along with \(\text{NH}_3\) in an atmospheric pressure CVD experiment to obtain an amorphous \(\text{Si}_3\text{N}_4\) film at 600 °C.

A second thrust area has involved the preparation of thin films of aluminum nitride and the cuprate superconductors by solution deposition methods using polymeric precursors. In the case of AlN, we have investigated the interaction of triethyl- and trimethylaluminum with ethylenediamine and have obtained evidence for several novel intermediates including polymeric derivatives which can be used to make fibers and thin films. Pyrolysis of these films under ammonia was found to give thin, apparently dense, AlN films on Si and other substrates. Our preparation of
the cuprate superconductor films has employed the citric acid/
ethyleneglycol system as a source of both the \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) (1-2-3) and
\( \text{Bi/Sr/Cu/O} \) superconductors via solution deposition followed by pyrolysis.
Efforts here have focused on the evolution of the cuprate superconductor
phases from the polymeric precursor system and have involved the use of IR,
TGA, XRD and other methods to follow the conversion process. Successful
deposition of "1-2-3" films on \( \text{ZrO}_2 \) and \( \text{Al}_2\text{O}_3 \) substrates was demonstrated,
by several successive dip-coatings with the precursor solution followed, in
each case, by pyrolysis to 500 °C in air with a final anneal in oxygen at
950 °C. The intermediate formation of an intimate mixture of \( \text{Y}_2\text{O}_3 \), \text{CuO} and
\( \text{BaCO}_3 \) on pyrolysis of the "1-2-3" precursor system, followed by conversion
to the "1-2-3" orthorhombic phase at ca. 850 °C, was evidenced by the XRD
data.

The results of these studies have been summarized in twelve papers
published or submitted for publication and numerous presentations at
scientific meetings and universities. A list of these papers and the
meeting presentations follows.

**Papers Published or Submitted for Publication under the Contract**

1. L.V. Interrante, L.E. Carpenter, C. Whitmarsh, W. Lee, G.A. Slack, and
M. Garbauskas, "Studies of Organometallic Precursors to Aluminum Nitride",

2. L.V. Interrante, W. Lee, M. McConnell, N. Lewis, and E. Hall,
"Preparation and Properties of Aluminum Nitride Films Using an

3. L.V. Interrante, Z. Jiang, and D.J. Larkin, "Preparation of the High-Tc
Superconductor \( \text{YBa}_2\text{Cu}_3\text{O}_{7-x} \) Using Organometallic Precursors", *ACS Symposium

4. L.V. Interrante, C. Czekaj, and W. Lee, "CVD of AlN and SiC Thin
Films Using Designed Organometallic Precursors", NATO ASI Proceedings,
"Mechanisms of Reactions of Organometallic Compounds with Surfaces", D.J.

5. W. Lee, L.V. Interrante, C. Czekaj, J. Hudson, K. Lenz, and B-X. Sun,
"Chemical Vapor Deposition of Silicon Carbide Using A Novel Organometallic


Books Edited

Presentations at Scientific/Technical Conferences (all invited, except as noted)


1989.


Chairing of Meetings


Graduate Students Supported Under the Contract

Wei Lee (M.S. 1988)
Zhiping Jiang (Ph.D. December 1990, currently at MIT Ceramics Res. Lab)
Donna Narsavage (Ph.D. expected, June 1991)
David Larkin (Ph.D. expected, June 1991)
APPENDIX A

The construction and testing of a cold-wall, hot-stage LPCVD reactor was completed during the period of this research contract. The apparatus consists of a stainless steel chamber containing a 2" diameter electrically heated hot stage interfaced with a precursor vapor source and a vacuum system. In experiments involving the use of single crystal Si as a substrate, the hot stage was replaced by Cu wire leads (terminating in W and Ta clips) for direct resistive heating of the substrate. The Cu leads were connected to an external DC current limited power supply.

The vacuum system includes a turbomolecular pump backed by a two-stage, rotary vane mechanical pump. The operating pressure in the reactor is controlled by an electronically operated butterfly valve between the pumping system and the reactor chamber. A capacitance manometer senses the reactor pressure and, when required, automatically controls the butterfly valve to maintain a constant system pressure. A system of electropneumatic actuated valves and pressure feedback loops provide protection for the turbopump and operator in the event of power failure or operator error.

This apparatus has been interfaced recently with a 200 amu quadrupole mass spectrometer (Hyden Analytical) and a mass flow controller, permitting accurate control of precursor admission rates and on-line analysis of the volatile gaseous products. A diagram which illustrates the main components of this CVD apparatus and their configuration follows.
Figure  A schematic of the LPCVD system with an attached QMS; 1.) Carrier gas inlet, 2.) Mass flow controller, 3.) Stainless bubbler containing precursor, 4.) Capacitance manometer, 5.) Saphire view port, 6.) Silicon substrates, 7.) Series of 3 cold traps, 8.) Sampling leak valve, 9.) QMS, 10.) Mechanical pump used to maintain the gas sample flow, 11.) to the LPCVD main L-N$_2$ cooled trap and pumping system.