

## Conference Report

## Molecular Routes to Materials in New York

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A symposium entitled "Molecular Routes to Materials" was held in New York City at the 4th Chemical Congress of the North American Continent in August, 1991. The talks focused on synthetic and mechanistic studies of the formation of metals, borides, nitrides, carbides, oxides, and compound semiconductors from molecular precursors.

Dr. Joel Miller (DuPont) outlined recent success in obtaining magnetic materials from molecular organometallic precursors. The crystalline product obtained from the reaction between decamethylferrocene and TCNE consisted of stacks of alternating cation and anion radicals. The material becomes magnetically ordered at low temperature ( $T_c = 4.8$  K) to give a molecular ferromagnet that has a higher saturation magnetization than metallic iron. During the investigation of related complexes, the reaction of bisbenzenevanadium with TCNE yielded an air-sensitive, amorphous black powder. Although the structure of this material is unknown, both benzene ligands were replaced with interactions between TCNE and vanadium. This solid was found to exhibit ferromagnetic behavior well above room temperature and more studies are underway to establish the structure of the compound.

Mössbauer spectroscopy was utilized to probe the magnetic behavior of thin films of iron boride glasses prepared using molecular metal carbonyl clusters containing boron. In this work, Thomas Fehlner (Notre Dame) established a relationship between the Fe/B ratio in the thin film and the Fe/B ratio of the precursor. For example,  $\text{Fe}_2(\text{CO})_6(\text{B}_2\text{H}_6)$  led to FeB. The small amount of oxygen present in these films was shown to be present as  $\text{B}_2\text{O}_3$ .

New synthetic routes to nanocrystalline phosphides of zinc, cadmium, gallium, and indium were described by William Buhro (Washington Univ.). Molecular metal silylphosphido complexes (e.g.  $\text{Cd}[\text{P}(\text{SiPh}_3)_2]_2$ ) were typically used as precursors. These compounds react with alcohols to form the soluble silyl ether and unsubstituted phosphido ( $\text{PH}_2$ ) complexes which further react to give nanocrystalline materials such as  $\text{Cd}_3\text{P}_2$ . An alternative route to  $\text{Cd}_3\text{P}_2$  involving the reaction of  $\text{P}(\text{SiMe}_3)_3$  with metal alkoxides such as  $\text{Cd}[\text{OCH}(\text{Me})\text{CH}_2\text{NMe}_2]_2$  was described. Transmission electron microscopy was used to establish that the  $\text{Cd}_3\text{P}_2$

particles were 30 Å in diameter while corresponding  $\text{Zn}_3\text{P}_2$  particles grew to 50 Å. The reaction of alcohol with the pyridine adduct of  $\text{In}[\text{P}(\text{SiMe}_3)_2]_3$  again resulted in the replacement of the P-SiMe<sub>3</sub> bonds with P-H bonds. Phosphine elimination occurred along with the formation of amorphous InP.

Metal nitrides of both transition and nontransition elements were the subject of several talks and it is noteworthy that ammonia was the ultimate nitrogen source in each study. David Hoffman (University of Houston) described work done in a collaboration with Roy Gordon at Harvard on the growth of thin films of metal nitrides in an ammonia atmosphere at temperatures between 200 and 400 °C using amido complexes of a variety of metals. This included using  $\text{Sn}(\text{NMe}_2)_4$  to form the previously uncharacterized phase  $\text{Sn}_3\text{N}_4$ . Forward recoil spectroscopy was utilized to quantify the hydrogen content of the films. Hydrogen was always present and in some cases nearly as abundant as the metal itself. Because hydrogen is so difficult to detect by most methods, forward recoil spectroscopy will become an increasingly important technique to characterize solids synthesized at relatively low temperatures.

Peter Wolczanski (Cornell) described the reaction of ammonia with melts of tris[bis(trimethylsilyl)amido]lanthanide complexes. Crystalline nitrides were ultimately obtained after heating the initially formed nitrides to 575 °C. Adding  $\text{LiNH}_2$  or  $\text{LiCl}$  to the initial mixtures resulted in improved crystallinity perhaps by acting as a flux growth medium. Initial members of a new family of molecular complexes labelled polyamidoimidonitrides (PAIN) were isolated during the controlled reaction of  $\text{Zr}[\text{OC}(\text{CMe}_3)_3](\text{CH}_2\text{Ph})_3$  with ammonia. Compounds such as the square pyramidal cluster,  $\text{Zr}_5(\text{OR})_5(\text{NH}_2)_4(\text{NH})_4(\text{N})$ , bear a striking structural resemblance to polyoxoanions.

The preparation of the first samples of cubic gallium nitride was reported by Wayne Gladfelter (University of Minnesota) to proceed via a topochemical solid-state reaction starting with cyclotrigallazane,  $[\text{H}_2\text{GaNH}_2]_3$ . In the solid state, the chair conformation of this six-membered ring stacks in a pattern that mimics the zinc blende structure. At 150 °C under argon, hydrogen elimination occurs with concomitant formation of new Ga-N bonds, and by 600 °C the thermodynamically less-stable phase *cubic* GaN is isolated. The average diameter of the crystallites was established to be 60 Å using X-ray line widths and TEM. Under high resolution, the TEM images also resolved the individual lattice planes of the structure.

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Another cyclic precursor,  $[R^1R^2SiCH_2]_2$  where R = Me or H, was reported by Leonard Interrante Rensselaer Polytechnic Institute to form thin films of silicon carbide in a LPCVD reactor between 700–1100 °C. The carbon-to-silicon ratio of the films was dependent on both the formula of the precursor and on the temperature of the deposition. For instance,  $[Me_2SiCH_2]_2$  yielded carbon-rich films up to 1100 °C, whereas  $[H_2SiCH_2]_2$  produced a silicon-rich phase at low temperature and stoichiometric SiC above 800 °C.

Complementing the discussion of novel precursor chemistry was a series of talks focusing on measuring the kinetics and probing the gas phase and surface reaction mechanisms of CVD processes. Bruce Scott (IBM) described experimental studies of the use of silane and disilane for growing thin epitaxial films of silicon. By varying the conditions of the deposition, especially total pressure and silane partial pressure, the gas phase chemistry could be controlled to allow either the original precursor ( $SiH_4$ ) or a partially reacted fragment ( $SiH_2$ ) to be the predominant growth species.

The importance of gas-phase chemistry in CVD processes such as silicon or silicon nitride growth has prompted the development of models that combine fundamental chemical rate constants for important reactions with a detailed hydrodynamic description of the fluid flow in the reactor. The research described by Pauline Ho (Sandia National Labs) focused on some of the spectroscopic methods used to extract the fundamental constants necessary to describe quantitatively a given CVD process. For instance, silicon hydride ( $SiH$ ) generated from a silane plasma was found to react nearly quantitatively with a partially hydrogenated silicon surface.

Richard Masel (Illinois) described the chemistry of various gallium methyl complexes on indium phosphide surfaces. Temperature programmed desorption studies established that  $GaMe_3$ ,  $GaMe_2$ , and  $GaMe$  desorb from InP surfaces that have been dosed with  $GaMe_2$ . Similar scrambling of the methyl groups occurred upon adsorption of  $GaMe$  on InP surfaces. Of particular importance was the observation that  $GaMe_3$  reacts with stainless steel surfaces slightly above room temperature. At 350 K, pure gaseous  $GaMe_3$  is converted into a nearly 1:1 mixture of  $GaMe_2$  and  $GaMe_3$ . Because virtually all MOCVD systems transport  $GaMe_3$  through steel lines, this finding suggests that intact  $GaMe_3$  may never reach the substrate. Under similar conditions, quartz surfaces had no effect on the  $GaMe_3$ .

The surface kinetics and mechanisms of the CVD of aluminum using triisobutylaluminum and various tertiary amine complexes of alane was the subject of the talk by Larry Dubois (AT & T Bell Laboratories). The rate determining step for aluminum growth using triisobutylaluminum involves  $\beta$ -hydrogen elimination of isobutene. Subsequent desorption of isobutene and hydrogen is rapid. Aluminum films can also be grown from the alane precursor  $Me_3NAIH_3$ ; in this case the rate determining step is dissociation of the Al–N bond. Even the subtle change to  $Et_3NAIH_3$ , however, changes the rate determining step to

the elimination of hydrogen from the surface. The surface morphology was monitored during film growth by helium scattering. It was found that during growth on a single crystal of aluminum, the surface actually became smoother.

The use of organometallic precursors for the deposition of copper is being actively investigated due to the potential advantages of copper as the material of choice (rather than tungsten or aluminum) for vias in integrated circuits. David Beach (IBM) described the deposition of copper films at 150–200 °C from the cyclopentadienyl precursor  $(C_5H_5)Cu(PEt_3)$ . The films grew selectively on transition metal surfaces at rates of 500–600 Å/min, contained only about  $10^{15}$  oxygen and carbon atoms per  $cm^3$ , and exhibited electrical resistivities below  $2 \mu\Omega\text{-cm}$ . The grain sizes were typically ca. 0.6  $\mu m$ , and vias with 3:1 aspect ratios could be filled completely. There is, however, evidence of a wall-poisoning effect which greatly decreases the film growth rates onto fresh substrates placed into a previously used deposition chamber.

Mark Hampden-Smith (University of New Mexico) described the selective deposition of similar high-quality copper films at rates of 70–210 Å/min by the passage of copper(I) hexafluoroacetylacetonate complexes such as  $Cu(hfac)(PMe_3)$  over tungsten-, copper-, or platinum-coated silicon wafers at temperatures between 200 and 250 °C. Kinetic studies yielded an activation energy of 26(2) kcal/mol for the deposition, and a mechanism involving disproportionation of the copper(II) precursor to copper metal and the copper(II) hexafluoroacetylacetonate complex has been proposed.

Gregory Girolami and Patrick Jeffries (University of Illinois at Urbana-Champaign) described their mechanistic studies of the deposition of copper and copper(I) oxide from the *tert*-butoxide complex  $[Cu(O\text{-}t\text{-}C_4H_9)]_4$ . At temperatures below 200 °C, an elimination reaction occurs to give exclusively copper(I) oxide and the organic products isobutene and *tert*-butanol; at higher temperatures, copper(I) oxide is formed as an intermediate and apparently loses oxygen under low-pressure CVD conditions to generate copper metal. Ultrahigh vacuum studies on single crystal Cu(110) surfaces support these mechanisms.

Mihal Gross (AT & T Bell Laboratories) utilized thermogravimetric analysis to assess the decomposition reactions of potential CVD precursors for copper. The tetrameric complexes  $[Cu(O\text{-}t\text{-}C_4H_9)]_4$  and  $[Cu(CO)(O\text{-}t\text{-}C_4H_9)]_4$  exhibit a final weight loss at 245 and 260 °C, respectively. The latter complex also exhibits a weight loss at lower temperature attributable to CO loss. Related studies suggested that mixed alkoxide fluoroalkoxide complexes such as  $[Cu(O\text{-}t\text{-}C_4H_9)_{0.6}(O\text{-}t\text{-}C_4F_9)_{0.4}]_4$  may also prove to be useful precursors for copper deposition.

Herb Kaesz (UCLA)<sup>[1]</sup> described growth rate studies of the deposition of platinum from  $(C_5H_4CH_3)Pt(CH_3)_3$  under hydrogen; the presence of an induction period followed by a period of rapid film deposition strongly suggests that platinum deposition is autocatalytic. Richard Puddephatt (Uni-

versity of Western Ontario) has observed that platinum deposition from the isonitrile complex  $\text{Pt}(\text{CH}_3)_2(\text{CNCH}_3)_2$  under nitrogen also occurs after an initial induction period. The deposition kinetics thereafter are non-first-order in both platinum precursor and in hydrogen; the deposition is inhibited by methylisonitrile but accelerated by light. Single-crystal ultra-high-vacuum studies of the deposition process show that  $\text{CNCH}_3$  groups from the precursor migrate onto the  $\text{Pt}(111)$  surface upon dosing, even at 110 K. Subsequent hydrogenolysis of the  $\text{Pt}-\text{CH}_3$  groups yields methane.

Alan Cowley described work done in collaboration with Richard Jones and John Eckerdt at the University of Texas at Austin on the chemical vapor deposition of gallium arsenide from organometallic precursors. Films of GaAs can be grown epitaxially on GaAs(100) at 550 °C and  $10^{-4}$  torr at rates of 1  $\mu\text{m/hr}$  from molecules of stoichiometry  $[\text{R}_2\text{GaAsR}'_2]_x$ . The films possess a band gap of 1.43 eV as judged from the photoluminescence spectra, and carbon is not detectable by SIMS.

The deposition of zinc selenide at 350–500 °C by MOCVD from dimethylzinc and several organoselenium precursors was described by Klavs Jensen (MIT). All the films grown above 350 °C exhibit the  $\text{Y}_0$  defect as determined by photoluminescence spectroscopy. High levels of carbon ( $> 10^{21}$  atoms/ $\text{cm}^3$ ) were seen in the films if (allyl)(methyl)selenium was used as the selenium precursor; in contrast, diethylselenium and di(allyl)selenium gave relatively carbon-free films. Significantly, however, the latter precursor allows the deposition of ZnSe to be conducted at 425 °C, vs. 500 °C for diethylselenium. It was also reported that the amine adduct  $\text{Zn}(\text{CH}_3)_2 \cdot \text{N}(\text{CH}_3)_3$ , which has been studied at the Royal Signals and Radar Establishment (RSRE) in Great Britain, gives much smoother ZnSe films and offers processing advantages over dimethylzinc by inhibiting pre-reactions at low temperatures. Addition of ammonia to dimethylzinc/dialkylselenium gas streams gives films in which nitrogen has been incorporated into the Se sites.

John Arnold (University of California at Berkeley) described efforts to develop single-source CVD precursors to ZnTe, CdTe, and HgTe. Preliminary results suggest that ZnTe films can be grown on a quartz substrate at 325 °C and 1 atm from a nitrogen stream of the zinc tellurolate complex  $\text{Zn}[\text{TeSi}(\text{SiMe}_3)_3]_2$ .

Mike Steigerwald (AT & T Bell Laboratories) presented an overview of the nickel telluride cluster intermediates that are involved in the low-temperature synthesis of NiTe and  $\text{Ni}_3\text{Te}_2$  from  $\text{TeP}(\text{C}_2\text{H}_5)_3$  and the nickel cyclooctadiene complex  $\text{Ni}(\text{C}_8\text{H}_{12})_2$ . The nickel clusters  $\text{Ni}_{20}\text{Te}_{18}(\text{PET}_3)_{12}$  and  $\text{Ni}_9\text{Te}_6(\text{PET}_3)_8$  possess structures that may be regarded as portions of the NiTe lattice. In addition, the  $\text{Ni}_{20}$  cluster

possesses magnetic properties that presage the Pauli paramagnetism of the nickel telluride phases that can be obtained by heating the cluster to 100 °C.

The identification of titanium oxo/alkoxides that are intermediates in the sol-gel synthesis of  $\text{TiO}_2$  from titanium alkoxides was described by Walter Klemperer of the University of Illinois at Urbana-Champaign, in collaboration with Victor Day of the University of Nebraska. The  $^{17}\text{O}$  NMR spectra and several of the single-crystal X-ray structures of  $\text{Ti}_7\text{O}_4(\text{OR})_{20}$ ,  $\text{Ti}_8\text{O}_6(\text{OR})_{20}$ ,  $\text{Ti}_{10}\text{O}_8(\text{OR})_{24}$ ,  $\text{Ti}_{11}\text{O}_{13}(\text{OR})_{18}$ ,  $\text{Ti}_{12}\text{O}_{16}(\text{OR})_{16}$ , and  $\text{Ti}_{16}\text{O}_{16}(\text{OR})_{32}$  were described; of these, only the  $\text{Ti}_7$  and  $\text{Ti}_8$  clusters (and at least one other species) are present in significant amounts in solution during sol-gel condensation.

Toivo Kodas (University of New Mexico) detailed his studies of the vapor-phase synthesis of ceramic powders. Several of the superconducting copper oxide phases can be made by aspirating aqueous solutions of appropriate mixtures of the corresponding metal nitrates into a hot zone swept with a mixture of  $\text{O}_2$  and  $\text{N}_2$ ; the microdroplets are dried in the hot zone and undergo hydrolysis and oxidation while still suspended. The resulting particles can be collected and annealed under oxygen at 800 °C for 12 hours; this procedure has given single-phase samples of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  that are more dense and have smaller grains than samples prepared by most other routes. The superconducting transition has an onset temperature of 91 K and the samples can carry critical currents of  $10^5$  A/ $\text{cm}^2$ .

The synthesis of ceramic superconductors by MOCVD was described by Tobin Marks (Northwestern University). The Northwestern group has prepared  $\text{YBa}_2\text{Cu}_3\text{O}_7$  as well as the  $\text{Bi/Sr/Ca/Cu/O}$  and  $\text{Tl/Ba/Ca/Cu/O}$  phases by annealing MOCVD deposited films and in many cases the films are highly *c*-axis oriented when deposited on lattice-matched substrates. A zero-resistivity critical temperature of 113 K was achieved for  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  on a silver/ $\text{YSrZrO}_3$  substrate, which is the highest reported for any MOCVD deposited superconductor. Recently, a new pulsed plasma-assisted CVD method similar to atomic layer epitaxy has been developed, which has allowed superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  to be deposited directly at 680 °C with no subsequent annealing step. This as-deposited film had a critical temperature of 90.5 K and carried a critical current of  $10^5$  A/ $\text{cm}^2$ .

It is clear that the advances of the past several years are beginning to make a dent in the difficult task of understanding the relationship between the structures of molecular precursors and the atomic and microstructural features of the solid-state materials prepared from them.

[1] A. Zinn, B. Niemer, H. D. Kaesz, *Adv. Mater.* **1992**, *4*, 375.