

## Coordination chemistry routes to films for superconducting electronics

Tobin J. Marks

Department of Chemistry, the Materials Research Center, and the Science and Technology Center for Superconductivity, Northwestern University, Evanston, IL, 60208-3113, USA

### ABSTRACT

This contribution surveys the design, synthesis, characterization, and implementation of volatile metal-organic coordination complexes for the MOCVD (metal-organic chemical vapor deposition) growth of thin films of high temperature superconductors, lattice-matched dielectrics, and electro-optic materials. The central focus is on fluorinated and fluorine-free  $\beta$ -diketonate and  $\beta$ -ketoiminate complexes. Target materials include the YBCO ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ), BSCCO ( $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ ) and TBCCO ( $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ ) superconducting phases as well as  $\text{YAlO}_3$ ,  $\text{NdGaO}_3$ ,  $\text{PrGaO}_3$ ,  $\text{BaPbO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{Sr}_2\text{AlTaO}_6$ .

### INTRODUCTION

The advent of superconducting cuprates (HTS materials) with critical temperatures in excess of 77K has sparked intense worldwide interest in the fundamental science and technology of these unique substances. An interesting synthetic and device fabrication issue concerns possible routes to high-quality thin films of these and related metal oxide materials. In contrast to PVD (physical vapor deposition) film growth techniques such as sputtering, pulsed laser deposition, reactive evaporation, and molecular beam epitaxy, MOCVD offers the potential attraction of simple apparatus, amenability to large-scale/large-area film growth, conformal coating (attractive for trench and via filling; step coverage), high throughput, and growth under highly oxidizing conditions (1). However, MOCVD processes are crucially dependent upon the availability of metal-organic precursors having high and stable vapor pressure as well as appropriate reactivity for film growth. The development of such compounds has presented a major challenge, and the implementation of HTS MOCVD film growth processes has been consequently impeded by the paucity of useful precursors. This article surveys efforts at Northwestern to design, synthesize, characterize, and implement volatile metal complexes for the growth of HTS, dielectric, and electro-optic films by MOCVD processes.

### MOCVD PRECURSOR DESIGN ISSUES

An attractive strategy for producing volatile metal complexes is to minimize lattice cohesive energies by encapsulating the metal ion in a sterically saturating, nonpolar ligand environment (2). Ligand fluorination is known to further promote volatility. For large divalent and trivalent ions (especially  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Ba}^{+3}$ , and lanthanides) such requirements can only be satisfied with sterically encumbered, multidentate ligands. Other important considerations in precursor design include ease of synthesis, purification, and handling. Since solid precursors can undergo particle sintering during film growth (leading to varying surface area and vapor pressure characteristics, hence poor control of film stoichiometry), liquid precursors are also a worthwhile objective. All factors being equal, air-stable precursors are most useful since they are more conveniently manipulated and require less specialized apparatus.

To date,  $\text{Ba}^{+2}$  MOCVD precursors have presented the greatest challenge due to the small ionic charge-to-radius ratio and kinetic lability, which have complicated attempts to achieve stable ligation environments. As an illustration, the "first-generation"  $\beta$ -diketonate precursor  $\text{Ba}(\text{dpm})_2$  ( $\text{dpm}$  = dipivaloylmethanate) exists in a number of mono- and polynuclear forms, is difficult to purify, and exhibits poor, unstable (due to thermal decomposition) vapor pressure characteristics (3). Ligand design for  $\text{Sr}^{+2}$  and  $\text{Ca}^{+2}$  encapsulation has also been problematic, but somewhat less so than for  $\text{Ba}^{+2}$ . Initial efforts in this Laboratory focused on bulky, fluorinated  $\beta$ -diketonates and ancillary ligands which might further saturate the metal coordination sphere (2). Parallel studies focused on analogous, fluorine-free ligand structures, liquid precursors, and additional precursors for dielectric film growth.

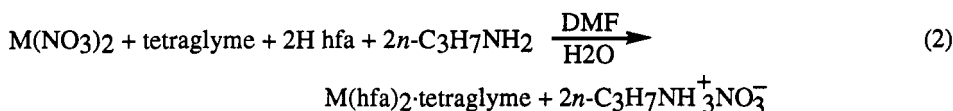
## SECOND GENERATION PRECURSORS

In 1988, we reported the low pressure MOCVD growth of YBCO films using  $\text{Ba}(\text{fod})_2$  (fod = heptafluorodimethyloctanedionate),  $\text{Y}(\text{dpm})_2$ , and  $\text{Cu}(\text{acac})_2$  (acac = acetylacetonate) as precursors and an Ar carrier gas with  $\text{H}_2\text{O}$  vapor and  $\text{O}_2$  as reactant gases (4). The role of the  $\text{H}_2\text{O}$  vapor was envisioned to be two-fold: i) protonolysis of metal- $\beta$ -diketonate linkages, ii) hydrolysis of  $\text{BaF}_2$  (identified by X-ray diffraction) which is a common thermolysis product of fluorinated barium  $\beta$ -diketonates (eq. (1)). In this early study, substrate temperatures were relatively low, and a post-anneal under flowing



$\text{O}_2$  to produce the superconducting phase not unexpectedly yielded films with rough surface morphologies. Nevertheless, X-ray diffraction (intense  $00l$  reflections) showed the films to be highly oriented (superconducting  $\text{CuO}_x$  planes parallel to the substrate surface) and phase-pure. Films on single crystal  $\text{SrTiO}_3$  and YSZ (yttrium-stabilized zirconia) exhibited  $T_c(\rho = 0)$  values as high as 87K, which were comparable to many PVD-derived films at that time (2).

The development of "second-generation" group 2 precursors having the formula  $\text{M}(\text{hfa})_2$ -polyether (M = Ca, Sr, Ba; hfa = hexafluoroacetylacetonate) represented a major advance in the field (5). These complexes are readily synthesized (eq. (2)) (6) and purified, invariably monomeric, and exhibit



high, relatively stable vapor pressure characteristics. The molecular structure of  $\text{Ba}(\text{hfa})_2$ -tetraglyme exhibits a distorted square antiprismatic coordination geometry with essentially "trans" hfa<sup>-</sup> ligands and the polyether encircling an equatorial "girdle" (Figure 1). Although analogous complexes with non-fluorinated ligands can be prepared, the diminished Lewis acidity of the metal ions apparently weakens the polyether binding -- decomposition occurs on attempted sublimation (7).

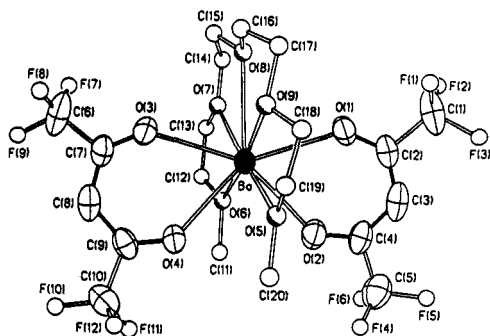


Fig. 1. Solid state structure of  $\text{Ba}(\text{hfa})_2$ -tetraglyme.

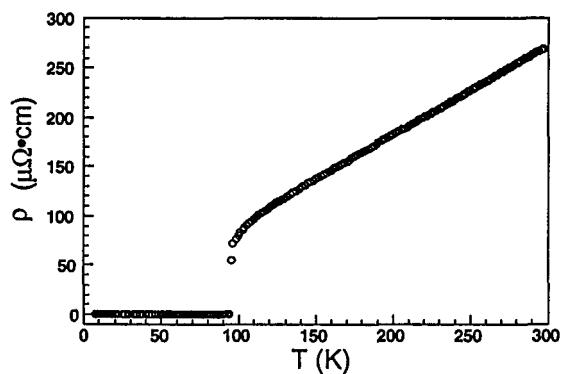


Fig. 2. Variable-temperature electrical resistivity data for a POMBE-derived YBCO film on (110)  $\text{LaAlO}_3$ .

YBCO film growth has been achieved using "second-generation" precursors ( $\text{Ba}(\text{hfa})_2$ -tetraglyme,  $\text{Y}(\text{dpm})_3$ ,  $\text{Cu}(\text{hfa})_2$ ) and the MOCVD variant, pulsed organometallic beam epitaxy (POMBE) (8). In this technique, precisely controlled pulses of the precursor vapors are directed at the substrate along with an oxygen plasma.  $\text{H}_2\text{O}$  vapor is again employed to remove fluoride. YBCO film growth can be achieved in situ (not requiring a post-anneal) at temperatures as low as  $700^\circ\text{C}$ . Typical POMBE-derived YBCO films grown on (110)  $\text{LaAlO}_3$  are phase-pure, highly oriented by X-ray diffraction  $\theta$ - $2\theta$  and  $\omega$  (rocking curve) scans, and highly epitaxial by in-plane  $\Phi$  scans. Atomic force microscopy indicates a surface roughness on the order of  $\pm 25\text{\AA}$ . Charge transport studies reveal these films to have  $T_c(\rho=0) = 93\text{K}$  (Figure 2), a critical current density,  $J_c = 5 \times 10^5 \text{ A/cm}^2$  in a 5T magnetic field (77K), and a film microwave surface resistance,  $R_s \approx 50\mu\Omega$  at 5K, 10GHz (9). These characteristics are comparable to those of the best PVD-derived YBCO films.

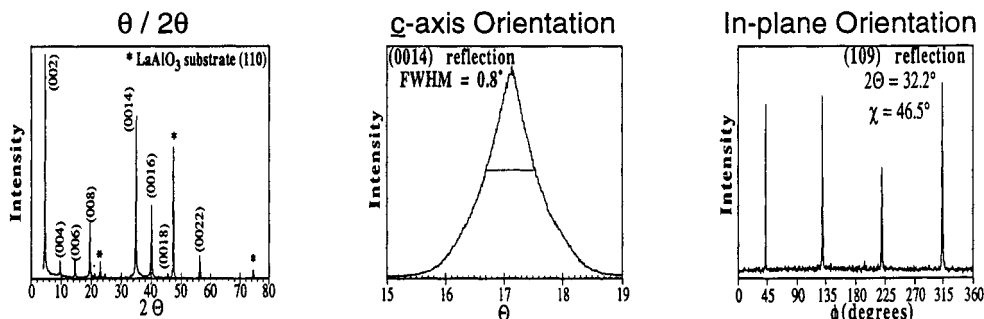


Figure 3. X-ray diffraction microstructural data for an MOCVD-derived TBCCO-2223 film on (110)  $\text{LaAlO}_3$ .

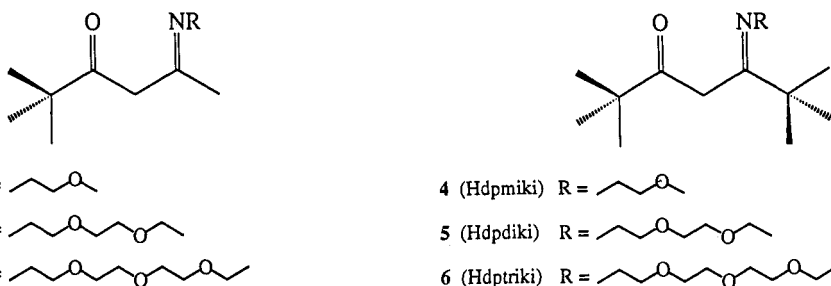
The pulsed mode of POMBE operation is particularly useful for forming complex, multi-component structures. Pulse sequences which alternate  $\text{Y}(\text{dpm})_3$  with  $\text{Pr}(\text{dpm})_3$  can be used to grow YBCO/PrBCO superlattices with alternating layers of the superconductor and semiconductor having precisely controlled thicknesses (8b). Both transmission electron microscopy and satellite reflections flanking the Bragg diffraction peaks indicate that the POMBE-derived superlattices have good structural regularity.

Second-generation precursors have also been employed to grow high-quality BSCCO films (10). Film growth using  $\text{Ca}(\text{hfa})_2$ -tetraglyme,  $\text{Sr}(\text{hfa})_2$ -tetraglyme,  $\text{Cu}(\text{acac})_2$ ,  $\text{Bi}(\text{C}_6\text{H}_5)_3$ , and an  $\text{O}_2/\text{H}_2\text{O}$  reactant gas mixture yields highly oriented, epitaxial  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  films on (110)  $\text{LaAlO}_3$  by an in situ process. The films exhibit surface roughness on the order of  $\pm 20\text{\AA}$ ,  $T_c(\rho = 0) = 90\text{K}$ , and  $J_c = 2.3 \times 10^5 \text{ a/cm}^2$  at 0T, 5K. These characteristics exceed those of any other BSCCO-2212 films grown by MOCVD to date and rival the best PVD - derived specimens.

The TBCCO HTS system offers a structurally diverse, environmentally robust family of HTS phases. Using second-generation precursors, it has been possible to selectively grow films of several of the TBCCO phases by MOCVD (5a,11). An example is  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  films, which can be grown on (110)  $\text{LaAlO}_3$  by low-pressure MOCVD techniques using  $\text{Ba}(\text{hfa})_2$ -tetraglyme,  $\text{Ca}(\text{hfa})_2$ -tetraglyme, and  $\text{Cu}(\text{hfa})_2$  as precursors and  $\text{H}_2\text{O} + \text{O}_2$  as reactant gases. As in most TBCCO film growth processes, a BCCO precursor film is first grown, followed by thallination in a second, post-anneal step (in this case, under flowing 10%  $\text{O}_2/\text{Ar}$ ). The resultant films are phase-pure, highly oriented, and epitaxial (Figure 3). Their high quality is evidenced by  $T_c(\rho = 0) = 115\text{K}$  (the highest to date for any MOCVD-derived HTS film),  $J_c = 6 \times 10^5 \text{ A/cm}^2$  at 0T, 77K, and by  $R_S = 0.35\text{m}\Omega$  at 5K, 10 GHz. These properties compare favorably with those of the highest quality PVD-derived TBCCO - 2223 films.

### FLUORINE-FREE AND LIQUID PRECURSORS

As noted above, the use of fluorine-containing precursors frequently results in film contamination by fluoride, which must be removed by additional processing which, in large-scale depositions, may be impracticable. Fluorine-free ligands were therefore designed in which a polyether "lariate" is appended to  $\beta$ -ketoiminate skeleton (1-6) (12). Barium complexes were then prepared in nonaqueous media using



$\text{BaH}_2$  as the metalating reagent (eq. (3)). A representative crystal structure (Figure 4; where  $\text{R} = \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ ) reveals an eight-coordinate, distorted dodecahedral configuration about

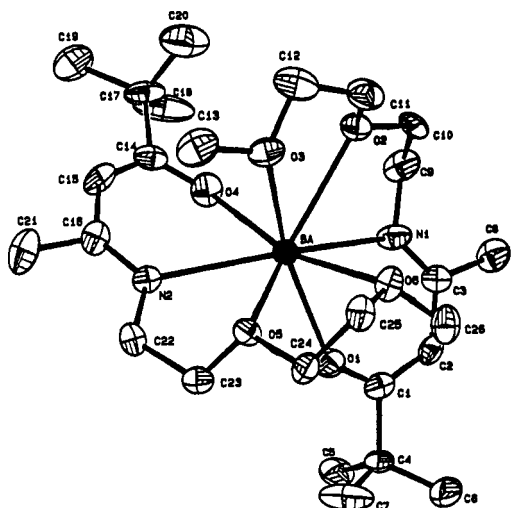


Fig.4. Solid state structure of the Ba<sup>2+</sup> complex of ligand **2**.

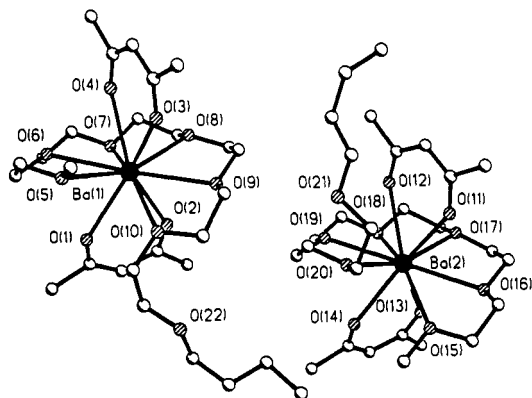
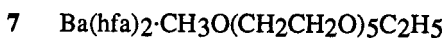
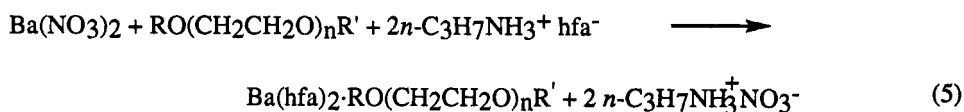
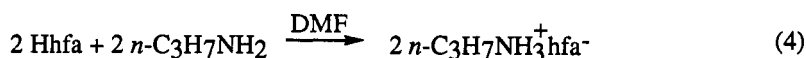


Fig. 5. Structures of the two crystallographically independent Ba<sup>2+</sup> complexes of ligand **8** in the solid state.

barium. In comparison to "Ba(dpm)<sub>2</sub>", these complexes exhibit greater volatilities and roughly comparable residues after complete sublimation. The efficacy in Ba transport has been illustrated via the MOCVD growth of films of the metal-like perovskite BaPbO<sub>3</sub> using one of these ketoiminates and Pb(dpm)<sub>2</sub> as precursors (12a). Thermolytic decomposition of these complexes involves cleavage of the C-O bond β to the ketoiminate nitrogen atom.

To date, the great majority of MOCVD precursors used in HTS film growth have been solids under growth conditions. As noted above, liquid precursors could offer potentially greater film growth efficiency and vapor pressure stability since there is more effective equilibration with the carrier gas stream and no unpredictable, sintering-dependent variation of vapor pressure characteristics. To address this problem, Ba(hfa)<sub>2</sub> polyether complexes have been prepared with a number of symmetry-breaking polyethers (e.g., eqs. (4),(5)) (13). Complexes **7** and **8** melt at 109-110° and 52-54°C, respectively,



versus 151-152°C for Ba(hfa)<sub>2</sub>-tetraglyme. The solid state structure of **8** consists of two crystallographically independent, 10-coordinate, distorted bicapped square antiprismatic molecules (Figure 5).

Low-pressure sublimation rate TGA experiments reveal that complex **7** sublimates ~ 3x more rapidly than Ba(hfa)<sub>2</sub>-tetraglyme under typical film growth conditions (120°C/6 Torr) (13). MOCVD experiments demonstrate that **3** can be used in combination with [Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>]<sub>n</sub> for the growth of epitaxial films of the electro-optic material BaTiO<sub>3</sub>. In regard to utility for high throughput film growth, complex **7** can be used nearly continuously over periods of months for MOCVD with negligible degradation in vapor pressure characteristics. In contrast, Ba(hfa)<sub>2</sub>-tetraglyme samples undergo significant reduction in volatility which can only be restored by interrupting the growth process and pulverizing the sintered specimens.

## MOCVD OF DIELECTRIC MATERIALS

For both passive and active HTS electronics, the ability to grow high-quality films of low dielectric constant, chemically inert, HTS lattice - and thermal expansion-matched dielectrics is of equal importance to that of growing HTS films. Such films are essential as substrates, buffers, interlayers, "seed layers", I components of SIS junctions, etc. MOCVD routes to orthorhombic  $\text{NdGaO}_3$  and  $\text{PrGaO}_3$  films employed rigorously purified  $\text{Nd}(\text{dpm})_3 + \text{Ga}(\text{dpm})_3$  or  $\text{Pr}(\text{dpm})_3 + \text{Ga}(\text{dpm})_3$ , respectively (14). In situ growth could be achieved on either (110)  $\text{LaAlO}_3$  or (001)  $\text{SrTiO}_3$   $\text{YAlO}_3$  could be grown in situ using  $\text{Y}(\text{dpm})_3$  and  $\text{Al}(\text{acac})_3$  in a similar procedure. X-ray diffraction reveals that these films are phase-pure, highly oriented, and epitaxial (15). HREM indicates atomically abrupt film-substrate interfaces and, interestingly, multiple film growth orientations ((001) and (110)); selected-area diffraction confirms the latter microstructure, which has also been observed in PVD-derived films. In related work, it has been shown that  $\text{PrGaO}_3$  films grown by MOCVD are excellent substrates for growth of high-quality epitaxial YBCO films by either pulsed laser deposition or POMBE (16).

$\text{Sr}_2\text{AlTaO}_6$  ("SAT") is of great current interest as a dielectric since it exhibits an excellent lattice and thermal expansion match with HTS materials, a low dielectric constant and loss tangent, and an absence of phase transitions between 77K and typical HTS film growth temperatures. Since SAT is cubic, there should be no problem with multiple growth orientations. In situ MOCVD of SAT films was achieved using rigorously purified  $\text{Al}(\text{acac})_3$ ,  $\text{Sr}(\text{hfa})_2$ -tetraglyme,  $\text{Ta}_2(\text{OCH}_2\text{CH}_3)_5$ , and  $\text{N}_2\text{O}$  as the oxidant gas.  $\text{H}_2\text{O}$  was not required, presumably because fluoride is removed from the films as volatile  $\text{TaF}_5$  (17). The films are phase-pure, highly oriented, and epitaxial by X-ray diffraction (Figure 6).

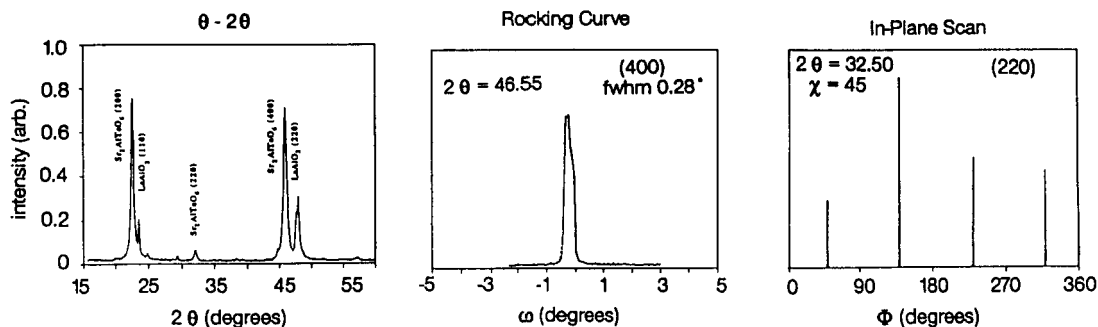


Fig. 6. X-ray diffraction microstructural data for an MOCVD - derived SAT film on (110)  $\text{LaAlO}_3$ .

Electron microscopy confirms epitaxy and reveals clean film-substrate interfaces with a single detectable growth orientation. The surface roughness is  $\sim \pm 70\text{\AA}$  by AFM. These specimens serve as satisfactory substrates for subsequent YBCO film growth (16b).

## CONCLUSIONS

The results summarized in this article highlight the status of MOCVD and related deposition techniques for the growth of high-quality HTS and related metal oxide thin films. Developing the coordination chemistry needed to produce efficient metal-organic MOCVD precursors has been a central focus of this activity, and one that has led to significant advances in the field. The next several years should witness further refinements in the precursor and film growth chemistry as well as the expeditious transition of film growth activities toward device-related structures.

## ACKNOWLEDGMENTS

The research described in this article was supported by the National Science Foundation through the Science and Technology Center for Superconductivity (Grant DMR 9120000) and the Northwestern Materials Research Center (Grant DMR 9120521), and by ARPA through contract 91-C-0112.

## REFERENCES

1. D.L. Schulz and T.J. Marks, *Adv. Mater.*, in press.
2. L.M. Tonge, D.S. Richeson, T.J. Marks, J. Zhao, J.M. Zhang, B.W. Wessels, H.O. Marcy, and C.R. Kannewurf, *Advances in Chemistry Series* **226**, 351 (1990).

3. L. Huang, S.B. Turnipseed, R.C. Haltiwanger, R.M. Barkley, and R.E. Sievers, *Inorg. Chem.* **33**, 798 (1994), and references therein.
4. J. Zhao, K.-H. Dahmen, H.O. Marcy, L.M. Tonge, T.J. Marks, B.W. Wessels, and C.R. Kannewurf, *Appl. Phys. Lett.* **53**, 1750 (1988).
5. (a) G. Malandrino, D.S. Richeson, T.J. Marks, D.C. DeGroot, J.L. Schindler, and C.R. Kannewurf, *Appl. Phys. Lett.* **58**, 182 (1991).  
(b) K. Timmer, K.D.M. Spee, A. Mackor, H.A. Meinema, A.L. Spek, and P. van der Sluis, *Inorg. Chim. Acta* **190**, 109 (1991).
6. D.L. Schulz, D.A. Neumayer, and T.J. Marks, *Inorg. Synth.*, in press.
7. R. Gardiner, D.W. Brown, P.S. Kirilin, and A.L. Rheingold, *Chem. Mater.* **3**, 1053 (1991).
8. (a) S.J. Duray, D.B. Buchholz, S.N. Song, D.S. Richeson, J.B. Ketterson, T.J. Marks, and R.P.H. Chang, *Appl. Phys. Lett.* **59**, 1503 (1991).  
(b) S.J. Duray, D.B. Buckholz, H. Zhang, S.N. Song, D.L. Schulz, V.P. Dravid, T.J. Marks, J.B. Ketterson, and R.P.H. Chang, *J. Vac. Sci. Technol. A* **11**, 1346 (1993).
9. D.C. DeGroot, T.P. Hogan, C.R. Kannewurf, D.B. Buchholz, R.P.H. Chang, F. Gao, M. Feng, and R.A. Nordin, *Physica C* **222** 271 (1994).
10. (a) J.M. Zhang, B.W. Wessels, D.S. Richeson, T.J. Marks, D.C. DeGroot, and C.R. Kannewurf, *J. Appl. Phys.* **69**, 2743 (1991).  
(b) J. Chen, H.A. Lu, F. DiMeo, Jr., B.W. Wessels, D.L. Schulz, T.J. Marks, J.L. Schindler, and C.R. Kannewurf, *J. Appl. Phys.* **73**, 4080 (1993).  
(c) F. DiMeo, Jr., B.W. Wessels, D.A. Neumayer, T.J. Marks, J.L. Schindler, and C.R. Kannewurf, *Mat. Res. Soc. Symp. Proc.* **335**, 285 (1994).
11. (a) D.S. Richeson, L.M. Tonge, J. Zhao, J. Zhang, H.O. Marcy, T.J. Marks, B.W. Wessels, and C.R. Kannewurf, *Appl. Phys. Lett.* **54**, 2154 (1989).  
(b) B.J. Hinds, D.L. Schulz, D.A. Neumayer, B. Han, T.J. Marks, Y.Y. Wang, V.P. Dravid, J.L. Schindler, T.P. Hogan, and C.R. Kannewurf, *Appl. Phys. Lett.* **65**, 231 (1994).
12. (a) D.L. Schulz, B.J. Hinds, D.A. Neumayer, C.L. Stern, and T.J. Marks, *Chem. Mater.* **5**, 1605 (1993), and references therein.  
(b) See also: W.S. Rees, Jr., C.R. Caballero, and W. Hesse, *Angew. Chem. Int. Engl. Ed.* **31**, 735 (1992).
13. D.A. Neumayer, D.B. Studebaker, B.J. Hinds, C.L. Stern, and T.J. Marks, *Chem. Mater.* **6**, 878 (1994).
14. (a) B. Han, D.A. Neumayer, D.L. Schulz, T.J. Marks, H. Zhang, and V.P. Dravid, *Appl. Phys. Lett.* **61**, 3047-3049 (1992).  
(b) B. Han, D.A. Neumayer, D.L. Schulz, B.J. Hinds, and T.J. Marks, *J. Vac. Sci. Technol. A* **11**, 1431 (1993).
15. B. Han, D.A. Neumayer, D.L. Schulz, B.J. Hinds, T.J. Marks, H. Zhang, and V.P. Dravid *Chem. Mater.* **5**, 14-16 (1993).
16. (a) B. Han, D.A. Neumayer, T.J. Marks, D.A. Rudman, H. Zhang, and V.P. Dravid, *Appl. Phys. Lett.* **63**, 3639 (1993).  
(b) B. Han, D.A. Neumayer, T.J. Marks, D.B. Buchholz, and R.P.H. Chang, manuscript in preparation.
17. B. Han, D.A. Neumayer, B.H. Goodreau, T.J. Marks, H. Zhang, and V.P. Dravid, *Chem. Mater.* **6**, 18 (1994).