

- [4] O. Takai, A. Hozumi, N. Sugimoto, *J. Non-Cryst. Solids* **1997**, *218*, 280.
 [5] Y. Wu, H. Sugimura, Y. Inoue, O. Takai, *Chem. Vap. Deposition* **2002**, *8*, 47.
 [6] F. Benitez, E. Martinez, J. Esteve, *Thin Solid Films* **2000**, *377*, 109.
 [7] R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988.
 [8] T. F. Schaub, G. J. Kellogg, A. M. Mayes, R. Kulasekera, J. F. Ankner, H. Kaiser, *Macromolecules* **1996**, *29*, 3982.
 [9] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, Y. Ueda, *Langmuir* **1999**, *15*, 4321.
 [10] T. Onda, S. Shibuichi, S. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125.
 [11] S. R. Coulson, I. Woodward, J. P. S. Badyal, S. A. Brewer, C. Willis, *J. Phys. Chem. B* **2000**, *14*, 8836.
 [12] K. Teshima, Y. Inoue, H. Sugimura, O. Takai, *Thin Solid Films* **2002**, *420*, 324.
 [13] G. Socrates, *Infrared Characteristic Group Frequencies*, 2nd ed., Wiley, Chichester, UK **1994**, pp. 188–194.
 [14] A. M. Wróbel, A. Walkiewicz-Pietrzykowska, Y. Hatanaka, S. Wickramanayaka, Y. Nakanishi, *Chem. Mater.* **2001**, *13*, 1884.

MOCVD Growth of Transparent Conducting Cd₂SnO₄ Thin Films**

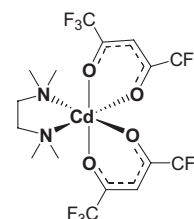
By Andrew W. Metz, Melissa A. Lane, Carl R. Kannewurf, Kenneth R. Poeppelmeier, and Tobin J. Marks*

Transparent conducting oxides (TCOs) are an important component of a great many opto-electronic device structures, including flat panel displays, organic light-emitting diodes (OLEDs), and photovoltaics (PVs).^[1] Tin-doped indium oxide (ITO) is the best known and most studied of these materials,^[2,3] but has severe limitations. The high price of indium, sub-optimal conductivity and transparency window, and chemical/interfacial instability in many PV^[4] and OLED^[5] structures, have stimulated a search for alternative materials. Cd₂SnO₄ has been the subject of intense investigation,^[6–11] exploring its potential as a low-cost, high-performance alternative to ITO, and Cd₂SnO₄ has been incorporated into PV device structures with promising results (efficiencies > 15 %).^[12,13]

Cd₂SnO₄ thin films have been prepared by several different growth techniques including radio frequency (RF) magnetron sputtering,^[9,10,13–16] RF reactive sputtering,^[6] pulsed laser deposition (PLD),^[17] dip coating,^[8,18] and sol-gel methods.^[19] As-deposited films produced by these techniques are often amorphous and require high temperature annealing to promote crystallization and to enhance opto-electronic properties. We are, however, unaware of reports of Cd₂SnO₄ film growth by metal-organic (MO)CVD in

the open literature. If possible, this would present an opportunity for large-scale process development that may be superior to/complement other film growth methods.

MOCVD is a widely used, large volume, thin film manufacturing process^[20] which complements physical vapor deposition techniques, and certain characteristics of MOCVD are particularly attractive for TCO thin film growth. These include growth conditions close to ambient, growth at relatively high O₂ partial pressures, conformal coverage over complex three-dimensional topologies, and amenability to very large-scale depositions with low cost apparatus. These attractions offer a technique suitable for maximum overall oxide growth efficiency and diverse applications. However, efficient growth requires highly volatile, thermally stable, easily handled metal-organic precursors. Until recently, there have been relatively few alternatives to highly toxic (more so than for typical Cd or Sn compounds),^[21] and pyrophoric,^[22] dimethylcadmium. We recently reported the first cadmium coordination complex, Cd(hfa)₂(TMEDA), to be successfully utilized as an efficient CdO MOCVD precursor.^[23]



Its attractive characteristics include a straightforward, one-step aqueous synthesis under ambient conditions from commercially available starting materials, excellent volatility, as well as excellent air and thermal stability. Further advances in cadmium precursor technology by our laboratory,^[24] and the complementary approaches of other groups,^[25] have resulted in an increased film growth capability for discovery, synthesis, and optimization of cadmium-containing opto-electronic materials. In this contribution, we report the first growth of transparent conducting Cd₂SnO₄ films by a MOCVD process. As-deposited, the films are highly crystalline on glass substrates at the relatively low growth temperature of 365 °C, and have electrical and optical properties rivaling those of commercial ITO.

CdO-SnO₂ films were grown on Corning 1737F glass (softening point = 975 °C) at 365 °C, and carrier gas ratios were adjusted until films with 2:1 Cd/Sn ratios (± 1 %) were obtained, as determined by inductively coupled plasma atomic-emission spectroscopy (ICP-AES). Films grown for 1.5 h have a thickness of 970 nm by profilometry (growth rate = 10.8 nm min⁻¹). The as-deposited films are highly crystalline with the cubic spinel Cd₂SnO₄ crystal structure,^[26] as determined by X-ray diffraction (XRD) θ - 2θ scans (Fig. 1). A small amount of CdO may be responsible for the broad (400) reflection at 39°. Scanning electron mi-

[*] Prof. T. J. Marks, Dr. A. W. Metz, Prof. K. R. Poeppelmeier
 Department of Chemistry, Northwestern University
 Evanston, IL 60208-3113 (USA)
 E-mail: t-marks@northwestern.edu
 Dr. M. A. Lane, Prof. C. R. Kannewurf
 Department of Electrical and Computer Engineering
 Northwestern University
 Evanston, IL 60208-3113 (USA)

[**] We thank the NSF MRSEC Program through the Northwestern Materials Research Center (DMR-0076097), NSF (CHE-0201767), and the DOE through the National Renewable Energy Laboratory (subcontract no. AAD-9-18668-05) for support of this research.

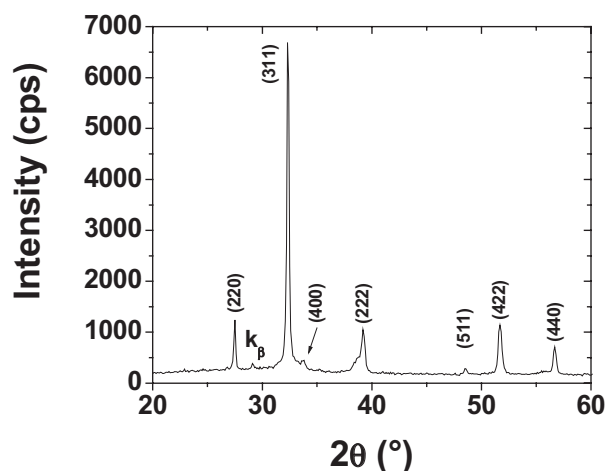


Fig. 1. XRD θ - 2θ scans of a MOCVD-derived Cd_2SnO_4 film deposited on glass at 365°C .

croscopy (SEM) images of the present MOCVD-derived Cd_2SnO_4 films (Fig. 2) reveal discrete grains with a relatively wide range of grain sizes, ~ 100 – 300 nm. Any fluorine contamination is below the energy dispersive X-ray spectroscopy (EDS) detection limits (1.5 at.-%).

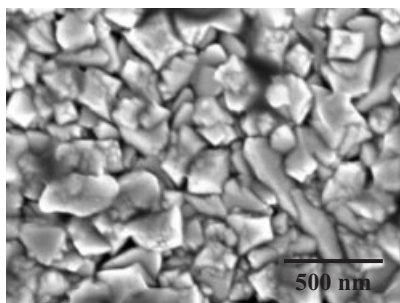


Fig. 2. SEM image of a Cd_2SnO_4 film deposited on glass at 365°C .

Figure 3 shows the charge transport characteristics of a MOCVD-derived Cd_2SnO_4 film as defined by variable-temperature Hall effect, and four-probe conductivity mea-

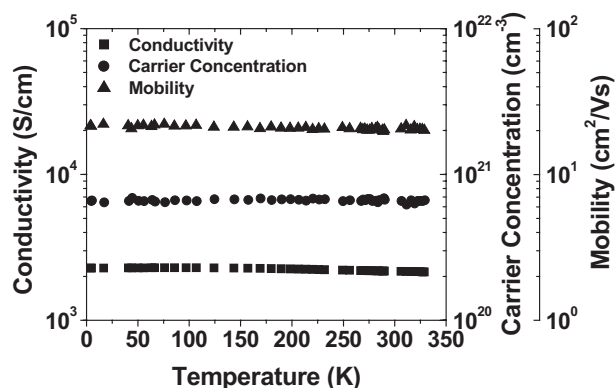


Fig. 3. Variable-temperature Hall effect and four-probe charge transport measurements for a Cd_2SnO_4 film deposited on glass at 365°C by MOCVD.

surements. The room temperature conductivity is 2170 S cm^{-1} with n-type carriers from the sign of the Hall coefficient. The corresponding room temperature carrier concentration and mobility are $6.64 \times 10^{20}\text{ cm}^{-3}$ and $20.3\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, respectively. Such temperature-independent carrier concentrations indicate degenerate semiconductor behavior,^[27] while the weak temperature dependence of the mobility argues for scattering by charged or neutral impurity centers.^[28] Optical transmittance spectra and a bandgap estimation plot^[29] for a MOCVD-derived Cd_2SnO_4 film are shown in Figure 4. Transmittance of $>85\%$ for the 970 nm thick film is observed over most of the visible region vs. the blank substrate. Although the intrinsic bandgap of Cd_2SnO_4 is quite small ($\sim 2.0\text{ eV}$),^[16]

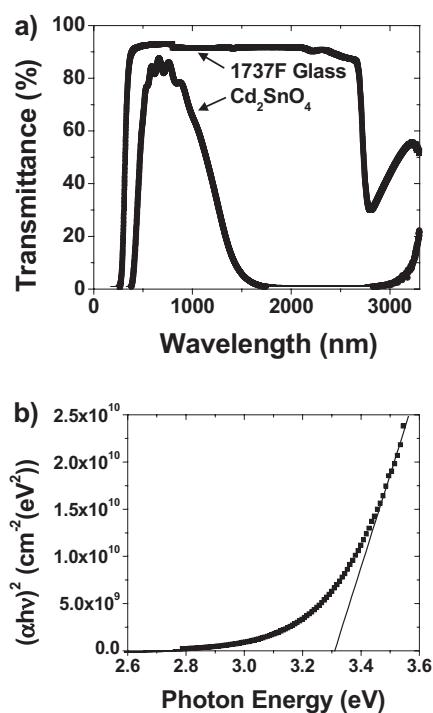


Fig. 4. Representative optical data for a Cd_2SnO_4 film deposited on glass at 365°C by MOCVD; film thickness = 970 nm. a) Optical transmission spectra. b) Bandgap estimation plot.

samples with high carrier concentrations display bandgaps greater than 3.0 eV , as a consequence of a carrier density-dependent Burstein–Moss shift.^[30] The band gap of the present sample is $>3.3\text{ eV}$, ample for most opto-electronic applications.^[2,31] The highest reported values for charge transport parameters of a Cd_2SnO_4 film (RF sputter-derived)^[9–11,13,14] are $\sigma = 8300\text{ S cm}^{-1}$, $n = 9.0 \times 10^{20}$, and $\mu = 59.6\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. However, these values could only be attained after an elaborate CdS/Ar annealing procedure. Typical reported conductivity values for other deposition techniques range from 1900 – 3500 S cm^{-1} (PLD)^[17] and 3000 S cm^{-1} (dip-coating).^[8]

In summary, Cd_2SnO_4 films have been grown for the first time by a MOCVD process. In contrast to most other de-

Table 1. MOCVD growth conditions for Cd₂SnO₄ thin films.

O ₂ (H ₂ O sat.) flow rate	300 sccm
Carrier gas (Ar) flow rates	40–80 sccm
Precursor reservoir temperatures	
Cd(hfa) ₂ (TMEDA)	85°C
ⁿ Bu ₂ Sn(TFA) ₂	50°C
Working pressure	6.70(5) torr
Substrate temperature	365°C
Substrate	Corning 1737F Glass

position methods, the films are highly crystalline as-deposited, alleviating the need for high temperature post-deposition annealing which would complicate large-scale device fabrication and possibly prohibit some substrates. Other groups have noted the importance of phase purity for maximum charge transport properties,^[9,32] and it is conceivable that removal of the trace amounts of the secondary CdO phase and/or additional optimization may further enhance charge mobility. At present, the charge transport properties of these Cd₂SnO₄ films are comparable to those of commercial ITO.

Experimental

Reagents: All reagents were used as received. Cd(NO₃)₂·4H₂O (99.999 % metal purity), *N,N,N',N'*-tetramethylethylenediamine, (ⁿBu₂SnO)₂, and trifluoroacetic acid were obtained from Aldrich. The ligand 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was obtained from Oakwood Chemicals. Cd(hfa)₂(TMEDA) [23] and ⁿBu₂Sn(TFA)₂ [33] were prepared by literature methods.

Film Growth and Characterization: MOCVD growth of Cd₂SnO₄ films was carried out using a previously described horizontal, cold-wall reactor [34]. During deposition runs, glass precursor reservoirs containing Cd(hfa)₂(TMEDA) and ⁿBu₂Sn(TFA)₂ were maintained at 80°C and 50°C, respectively. Carrier gas flow rates of 40–80 sccm of ultra-high purity Ar were passed through the thermostatted precursor reservoirs. The precursor stream was mixed with ultra-high purity O₂ (flowing at 300 sccm through a water bubbler) immediately upstream of the susceptor. A total working pressure of 6.70±0.05 torr was maintained during depositions. Corning 1737F glass substrates were obtained from Precision Glass and Optics and were cleaned with acetone, placed on the susceptor, dried in an oven at 105°C, and immediately placed in the susceptor holder of the laminar flow chamber of the MOCVD reactor. Film growth times were 1.5 h, and film thicknesses were measured with a Tencor P-10 step profilometer. Metal composition was determined by ICP-AES. Films were dissolved in a minimum of concentrated HCl and diluted for ICP analysis. XRD θ–2θ scans of the Cd₂SnO₄ films on glass were obtained with a Rigaku DMAX-A powder diffractometer using Ni-filtered Cu Kα radiation. Film surface microstructure was imaged with a Hitachi S4500 FE SEM equipped with a light element EDS. Variable-temperature Hall effect and four-probe conductivity data were collected between 4 K and 330 K using instrumentation described previously [35]. Optical transmittance spectra were acquired with a Cary 500 UV-vis-IR spectrophotometer and are referenced to the spectrum of the uncoated substrate.

Received: November 10, 2003
Final version: March 15, 2004

- [1] a) H. Hosono, H. Ohta, M. Orita, K. Ueda, M. Hirano, *Vacuum* **2002**, *66*, 419. b) Special issue on "Transparent Conducting Oxides", *MRS Bull.* **2000**, *25*(8), 15. c) Y. Akao, T. Haranoh, *Proc. 2nd Int. Conf. Coatings on Glass, High-Performance Coatings for Transparent Systems in Large-Area and/or High-Volume Applications* (Eds: H. K. Pulker, H. Schmidt, M. A. Ägerter), Elsevier Science, Amsterdam, The Netherlands **1999**, p. 338. d) S. H. Keshmiri, M. M. B. Mohaghe-

- ghi, S. O. Shir-Mard, M. R. Rokn-Abadi, *Proc. 13th Int. Conf. Surface Modification Technologies* (Eds: T. S. Sudarshan, K. Khor, M. Jeandin) ASM International, Materials Park, OH **1999**, p. 253. e) M. Saif, H. Patel, H. Memarian, *Proc. 10th Int. Conf. Vacuum Web Coating* (Ed: R. Bakish), Bakish Materials Corp., Englewood, NJ **1996**, p. 285.
- [2] C. G. Granqvist, A. Hultaker, *Thin Solid Films* **2002**, *411*, 1.
- [3] R. Bel Hadj Tahar, T. Ban, Y. Ohya, Y. Takahashi, *J. Appl. Phys.* **1998**, *83*, 2631.
- [4] A. Martel, F. Caballero-Briones, A. I. Oliva, R. Castro-Rodriguez, A. Iribarren, P. Bartolo-Perez, J. L. Pena, *Phys. Status Solidi B* **2000**, *220*, 261.
- [5] a) A. R. Schlatmann, D. W. Floet, A. Hilberer, F. Garten, J. M. Smulders, T. M. Klapwijk, G. Hadziioannou, *Appl. Phys. Lett.* **1996**, *69*, 1764. b) M. P. de Jong, L. J. van Ijzendoorn, M. J. A. de Voigt, *Appl. Phys. Lett.* **2000**, *77*, 2255.
- [6] W. L. Wang, K. J. Liao, C. Z. Cai, G. B. Liu, Y. Ma, *Surf. Coat. Technol.* **2003**, *167*, 284.
- [7] a) S. B. Zhang, S.-H. Wei, *Appl. Phys. Lett.* **2002**, *80*, 1376. b) D. R. Kammler, T. O. Mason, K. R. Poeppelmeier, *Chem. Mater.* **2000**, *12*, 1954.
- [8] R. B. H. Tahar, T. Ban, Y. Ohya, Y. Takahashi, *J. Am. Ceram. Soc.* **2001**, *84*, 85.
- [9] T. J. Coutts, D. L. Young, X. Li, W. P. Mulligan, X. Wu, *J. Vac. Sci. Technol., A* **2000**, *18*, 2646.
- [10] T. J. Coutts, X. Wu, W. P. Mulligan, J. M. Webb, *J. Electron. Mater.* **1996**, *25*, 935.
- [11] X. Wu, W. P. Mulligan, T. J. Coutts, *Thin Solid Films* **1996**, *286*, 274.
- [12] a) X. Wu, S. Asher, D. H. Levi, D. E. King, Y. Yan, T. A. Gessert, P. Sheldon, *J. Appl. Phys.* **2001**, *89*, 4564. b) X. Wu, R. G. Dhere, D. S. Albin, T. A. Gessert, C. DeHart, J. C. Keane, A. Duda, T. J. Coutts, S. Asher, D. H. Levi, H. R. Moutinho, Y. Yan, T. Moriarty, S. Johnston, K. Emery, P. Sheldon, *Proc.—NCPV Program Review Meeting 2001* (Eds: K. Ramanathan, S. Asher), National Technical Information Service, Springfield, VA **2001**, p. 47. c) X. Wu, R. Ribelin, R. G. Dhere, D. S. Albin, T. A. Gessert, S. Asher, D. H. Levi, A. Mason, H. R. Moutinho, P. Sheldon, *Conf. Rec. 28th IEEE Photovoltaic Spec. Conf.*, IEEE, Piscataway, NJ **2000**, p. 470.
- [13] T. J. Coutts, X. Wu, P. Sheldon, D. H. Rose, National Renewable Energy Lab., Golden, CO, <http://www.nrel.gov/ncpv/pdfs/coutts.pdf>, **1998**, p. 720.
- [14] X. Wu, T. J. Coutts, W. P. Mulligan, *J. Vac. Sci. Technol., A* **1997**, *15*, 1057.
- [15] T. J. Coutts, X. Wu, W. P. Mulligan, *Mater. Res. Soc. Symp. Proc.* **1996**, *426*, 479.
- [16] A. J. Nozik, *Phys. Rev. B: Solid State* **1972**, *6*, 453.
- [17] a) M. Yan, M. Lane, C. R. Kannevurf, R. P. H. Chang, *Appl. Phys. Lett.* **2001**, *78*, 2342. b) J. M. McGraw, P. A. Parilla, D. L. Schulz, J. Alleman, X. Wu, W. P. Mulligan, D. S. Ginley, T. J. Coutts, *Mater. Res. Soc. Symp. Proc.* **1995**, *388*, 51.
- [18] C. Ronconi, O. L. Alves, *Mol. Cryst. Liq. Cryst.* **2002**, *374*, 275.
- [19] a) G. Valincius, V. Reipa, V. Vilker, J. T. Woodward, M. Vaudin, *J. Electrochem. Soc.* **2001**, *148*, E341. b) H. Dislich, *Vide, les Couches Minces* **1985**, *40*, 261.
- [20] a) K. L. Choy, *Prog. Mater. Sci.* **2003**, *48*, 57. b) R. Waser, T. Schneller, S. Hoffmann-Eifert, P. Ehrhart, *Integ. Ferroelectr.* **2001**, *36*, 3. c) D. L. Schulz, T. J. Marks, in *CVD of Nonmetals* (Ed: W. S. Rees), VCH Publishers, New York **1996**, Ch. 2.
- [21] a) E. Y. Spiridonova, *Gig. Tr. Prof. Zabol.* **1991**, *14*, 4. b) J. K. Dunnick, B. A. Fowler in *Handbook on Toxicity of Inorganic Compounds* (Eds: H. G. Seiler, H. Sigel, A. Sigel), Dekker, New York **1988**, pp. 155–174.
- [22] A. D. Zorin, O. A. Emel'yanova, V. F. Zanozina, M. L. Markova, Y. N. Karataev, L. V. Stepanova, I. A. Feshchenko, *Zh. Prikl. Spektrosk.* **1989**, *51*, 903.
- [23] a) J. R. Babcock, A. Wang, A. W. Metz, N. L. Edleman, M. V. Metz, M. A. Lane, C. R. Kannevurf, T. J. Marks, *Chem. Vapor Deposition* **2001**, *7*, 239. b) J. R. Babcock, A. Wang, N. L. Edleman, D. D. Benson, A. W. Metz, M. V. Metz, T. J. Marks, *Mater. Res. Soc. Symp. Proc.* **2000**, *623*, 317.
- [24] A. W. Metz, J. R. Ireland, J. Ni, K. R. Poeppelmeier, C. R. Kannevurf, T. J. Marks, *Mater. Res. Soc. Symp. Proc.* **2002**, *721*, 165.
- [25] a) A. Gulino, P. Dapporto, P. Rossi, I. Fragalà, *Chem. Mater.* **2002**, *14*, 4955. b) A. Gulino, F. Castelli, P. Dapporto, P. Rossi, I. Fragalà, *Chem. Mater.* **2002**, *14*, 704. c) A. Gulino, P. Dapporto, P. Rossi, I. Fragalà, *Chem. Mater.* **2002**, *14*, 1441. d) M. Afzaal, D. Crouch, M. A. Malik, M. Motevallii, P. O'Brien, J.-H. Park, J. D. Woolins, *Eur. J. Inorg. Chem.* **2004**, *171*. e) M. Afzaal, S. M. Aucott, D. Crouch, P. O'Brien, J. D. Woolins, J.-H. Park, *Chem. Vapor Deposition* **2002**, *8*, 187.

- [26] a) M. E. Bowden, C. M. Cardile, *Powder Diffr.* **1990**, 5, 36. b) L. A. Siegel, *J. Appl. Crystallogr.* **1978**, 11, 284.
- [27] J. C. C. Fan, J. B. Goodenough, *J. Appl. Phys.* **1977**, 48, 3524.
- [28] a) N. Taga, H. Odaka, Y. Shigesato, I. Yasui, M. Kamei, T. E. Haynes, *J. Appl. Phys.* **1996**, 80, 978. b) R. B. Dingle, *Philos. Mag.* **1955**, 46, 831. c) C. Erginsoy, *Phys. Rev.* **1950**, 79, 1013. d) G. Frank, H. Koestlin, *Appl. Phys. A—Mater. Sci. Process* **1982**, A27, 197.
- [29] J. I. Pankove, *Optical Processes in Semiconductors*, Prentice-Hall, New York **1976**, Ch. 3.
- [30] a) I. Hamberg, C. G. Granqvist, *J. Appl. Phys.* **1986**, 60, R123. b) A. Wang, J. R. Babcock, N. L. Edleman, A. W. Metz, M. A. Lane, R. Asahi, V. P. Dravid, C. R. Kannewurf, A. J. Freeman, T. J. Marks, *Proc. Natl. Acad. Sci. USA* **2001**, 98, 7113.
- [31] B. G. Lewis, D. C. Paine, *MRS Bull.* **2000**, 25, 22.
- [32] G. Haacke, W. E. Mealmaker, L. A. Siegel, *Thin Solid Films* **1978**, 55, 67.
- [33] S. Suh, Z. Zhang, W.-K. Chu, D. M. Hoffman, *Thin Solid Films* **1999**, 345, 240.
- [34] B. J. Hinds, R. J. McNeely, D. B. Studebaker, T. J. Marks, T. P. Hogan, J. L. Schindler, C. R. Kannewurf, X. F. Zhang, D. J. Miller, *J. Mater. Res.* **1997**, 12, 1214.
- [35] J. W. Lyding, H. O. Marcy, T. J. Marks, C. R. Kannewurf, *IEEE Trans. Instrum. Meas.* **1988**, 37, 76.
-