# Chromium diboride thin films by low temperature chemical vapor deposition

Sreenivas Jayaraman, Emily J. Klein, and Yu Yang
*Department of Materials Science and Engineering, University of Illinois at Urbana Champaign, 1304 West Green Street, and Frederick Seitz Materials Research Laboratory, 104 South Goodwin Avenue, Urbana, Illinois 61801*

Do Young Kim and Gregory S. Girolami
*Department of Chemistry, University of Illinois at Urbana Champaign, 505 South Mathews Avenue and Frederick Seitz Materials Research Laboratory, 104 South Goodwin Avenue, Urbana, Illinois 61801*

John R. Abelson[a]
*Department of Materials Science and Engineering, University of Illinois at Urbana Champaign, 1304 West Green Street, and Frederick Seitz Materials Research Laboratory, 104 South Goodwin Avenue, Urbana, Illinois 61801*

(Received 11 January 2005; accepted 11 April 2005; published 7 June 2005)

Thin films of chromium diboride, a "metallic ceramic" material with a melting point of 2200 °C, were deposited by chemical vapor deposition using a single-source precursor, the bis(octahydrotriborato)chromium(II) complex $Cr(B_3H_8)_2$ at substrate temperatures as low as 200 °C. The films were stoichiometric, and had electrical resistivities of 105–450 $\mu\Omega$ cm for growth temperatures spanning a range of 200–400 °C. The film microstructure ranged from being x-ray amorphous at low growth temperatures to nanocrystalline for substrate temperatures >500 °C. The growth process was highly conformal, as determined by the film coverage profile on trenches with a depth–width ratio of 7:1. © *2005 American Vacuum Society.*
[DOI: 10.1116/1.1927534]

## I. INTRODUCTION

Transition metal diborides are "metallic ceramics" that have many desirable properties for technological applications, including excellent electrical conductivities, high melting points, low rates of impurity diffusion, high hardness, good resistance to mechanical wear, and low rates of corrosion.[1,2] For example, there has been recent work on the growth of zirconium diboride ($ZrB_2$) thin films by chemical vapor deposition (CVD) using the precursor tetrakis(tetrahydroborato)zirconium(IV), $Zr(BH_4)_4$. We have shown that amorphous films can be grown at low substrate temperatures, and that these films are effective diffusion barriers to separate copper and silicon in microelectronic circuits.[3] Tolle *et al.* have shown that highly oriented $ZrB_2$ layers can be grown on Si(111) substrates and that GaN films can be grown heteroepitaxially on the $ZrB_2$ template.[4]

In this work we focus on chromium diboride ($CrB_2$); this compound has a melting temperature of 2200 °C and a bulk hardness value of 22.5 GPa,[5] which makes it a promising material for hard coatings on cutting tools. Sputtered thin films of $CrB_2$ have exhibited excellent wear and corrosion resistance.[6] A bulk resistivity of 56 $\mu\Omega$ cm makes $CrB_2$ a candidate metal for microelectronic applications;[7] it has been tested successfully as an ohmic contact for SiC devices.[8]

In past work, $CrB_2$ films were grown using physical vapor deposition methods—sputtering or cathodic arc deposition—[6,9–11] which coat the substrate in a highly directional manner that is most suitable for planar substrates. However, a CVD process is required to produce a conformal coating over parts with complex shapes or re-entrant features, such as grooves or holes. In this work, we present a CVD route to afford high quality $CrB_2$ films: we employ a single source precursor, the bis(octahydrotriborato)chromium(II) complex $Cr(B_3H_8)_2$, to deposit stoichiometric, conformal films of $CrB_2$ at low substrate temperatures.[12] Note that the octahydrotriborate ($B_3H_8$) ligand is sterically much larger than the tetrahydroborate ligand ($BH_4$) associated with previously reported precursors[13,14] such as $Ti(BH_4)_3$ and $Zr(BH_4)_4$. Because of this steric bulk, a smaller number of ligands is required to enclose the metal center; consequently, this allows the formation of volatile molecules in which the metal center has a lower oxidation state, such as $Cr^{II}$ in this case. The ideal CVD reaction is expected to be $Cr(B_3H_8)_2 \rightarrow CrB_2 + 2B_2H_6 + 2H_2$.

## II. EXPERIMENT

The $Cr(B_3H_8)_2$ precursor is a solid at room temperature, and sublimes readily at 40 °C in vacuum. It is kept in a 60 $cm^3$ stainless steel reservoir at room temperature and delivered to the film growth surface using an 8.0 sccm flow of argon carrier gas through a 0.15 in. i.d. stainless steel dosing tube. This tube extends into the growth chamber, which is turbopumped and of ultrahigh vacuum construction,[15] and terminates 0.5–2.0 in. from the substrate; this distance is adjustable by substrate translation. The background pressure in the chamber is $5 \times 10^{-9}$ Torr; residual gas analysis indicates that most of this background is hydrogen. When the argon

[a]Electronic mail: abelson@mrl.uiuc.edu

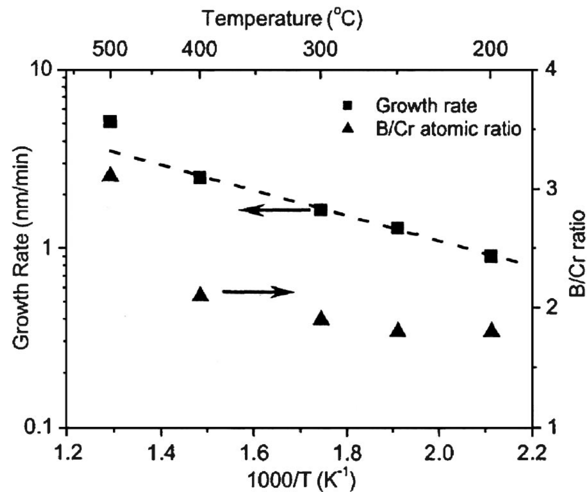


FIG. 1. Natural log of growth rate (left axis) and the B/Cr atomic ratio (right axis) vs $1000/T$ for the growth of $Cr(B_3H_8)_2$ by CVD. The dashed line is a linear fit to the growth rate data.

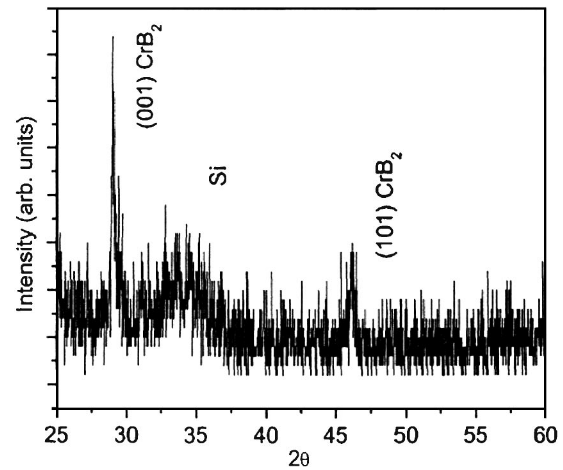


FIG. 2. X-ray diffraction pattern of the $CrB_2$ film grown by CVD at 700 °C.

carrier gas plus precursor is flowing, the chamber pressure is $6\times10^{-4}$ Torr in the absence of film growth (substrate at room temperature). Due to the use of a dosing tube, the precursor arrives at the substrate in a highly forward-directed flux,[16,17] and gas phase collisions or reactions are expected to be negligible. The substrate temperature is kept constant by means of a feedback loop consisting of a thermocouple clipped to the sample surface and a radiative heater behind the substrate holder. The substrates are 0.5 in. square pieces of Si(100) covered with 200 nm of $SiO_2$ that had been deposited in a separate plasma-enhanced CVD system.

Electrical resistivity measurements are performed using a four-point probe; there is no detectable leakage current between the $CrB_2$ film and Si substrate across the $SiO_2$. The film stoichiometry is measured *ex situ* by Auger electron spectroscopy using standard sensitivity factors and sputter depth profiling. The film thickness is measured from cross-sectional scanning electron microscope (SEM) micrographs.

## III. RESULTS AND DISCUSSIONS

Figure 1 shows the growth rate and the film stoichiometry versus substrate temperature for a fixed tube–substrate distance of 1 in.. For substrate temperatures $\leqslant 400$ °C, the growth rate is exponentially activated with an apparent barrier of 0.14 eV (3.22 kcal/mol), and the films have the stoichiometric $CrB_2$ composition. The oxygen and carbon contents are below the Auger detection limits. This is very different from the thermal CVD of $ZrB_2$ films[3] which have boron in excess of the stoichiometric amount at such low temperatures. This difference may be due to the reaction pathways of $BH_4$ versus $B_3H_8$ ligands on the growth surface. The $CrB_2$ film grown at 500 °C shows an excess of B and an increase in the growth rate above the value that would be extrapolated from lower temperatures. The mechanism(s) responsible for these changes are not understood at present. The films grown below 500 °C were amorphous to x-ray diffraction. Not shown in the growth rate plot is the result of a growth experiment at 700 °C using a slightly larger (1.5 in.) doser to substrate distance. That film is nanocrystalline with a grain size of ~67 nm as determined by Scherrer analysis of the x-ray diffraction peaks (Fig. 2). The electrical resistivity of the amorphous films ranged from 105 to 450 $\mu\Omega$ cm. The lowest value was measured for the film deposited at 200 °C.

At low deposition temperatures ($T\leqslant 300$ °C) the film growth is highly conformal. Figure 3 shows the coating profile for a film grown at 300 °C on a 200 nm wide trench with a depth/width aspect ratio of 7:1; the coating thickness on the sidewall and bottom is very uniform and amounts to ~55% of the thickness on the top surface. However, this coating profile, thicker on the top and uniformly thinner within the trench, does not correspond to the usual situation in which the growth is limited by the surface reaction rate, and is therefore largely independent of the incident flux. Here, the growth flux emanating from the doser tube is forward directed; if the growth rate were strongly flux dependent, then

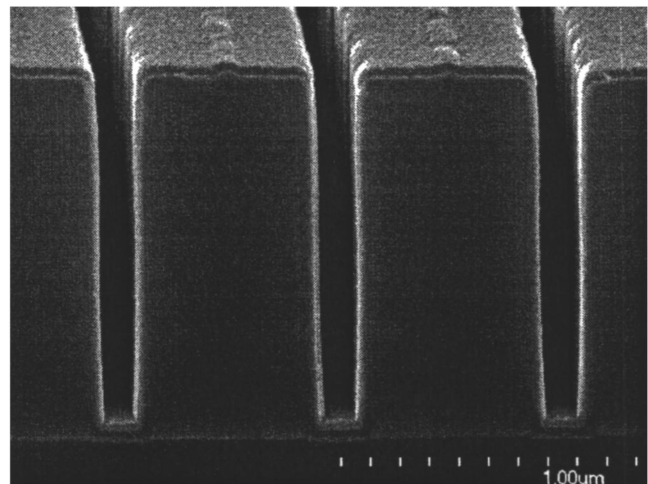


FIG. 3. Cross-sectional SEM image of $CrB_2$ film on 7:1 aspect ratio trenches in $SiO_2$ on silicon. The bumps on the surface were present on the substrate prior to the deposition

the profile we observe would be qualitatively reasonable. We obtained preliminary evidence for a flux dependence by coating an identical trench at a temperature of 200 °C using a smaller (0.5 in.) tube–substrate distance, and therefore a much higher flux. In this case, the growth rate on the top surface (2 nm/min) is much higher than the value (0.9 nm/min) given in Fig. 1 for 200 °C, and the film thickness is much greater on the top surface compared with the trench sidewall and bottom (~40% coverage). This film remains stoichiometric. Such flux dependence of the deposition rate at low substrate temperature implies that the growth kinetics are more complex than the "surface reaction rate limited" regime of CVD. Therefore, it is inappropriate to interpret the apparent activation energy of 0.14 eV cited above as representative of a single rate limiting process.

These results show that conformal, stoichiometric, and highly conductive thin films of $CrB_2$ can be grown by CVD at substrate temperatures as low as 200 °C using the recently synthesized precursor $Cr(B_3H_8)_2$. Further studies are planned to determine the surface chemistry, microstructural evolution, and mechanical properties of these films. The low temperature process should allow $CrB_2$ films to be deposited onto temperature-sensitive substrates such as polymers.[18]

## ACKNOWLEDGMENTS

The authors are grateful to the National Science Foundation for support of this research under Grant No. NSF CH00-76061. Compositional and structural analyses of the films were carried out in the Center for Microanalysis of Materials, University of Illinois, which is supported by the U.S. Department of Energy under Grant No. DOE DEFG02-91ER45439.

[1]J. Castaing and P. Costa, in *Boron and Refractory Borides*, edited by V. I. Matkovich (Springer, New York, 1977).
[2]C. Mitterer, J. Solid State Chem. **133**, 279 (1997).
[3]J. W. Sung, D. M. Goedde, G. S. Girolami, and J. R. Abelson, J. Appl. Phys. **91**, 3904 (2002).
[4]J. Tolle, R. Roucka, I. S. T. Tsong, C. Ritter, P. A. Crozier, A. V. G. Chizmeshya, and J. Kouvetakis, Appl. Phys. Lett. **82**, 2398 (2003).
[5]R. Kieffer and F. Benesovsky, *Hartstoffe* (Springer, New York, 1963).
[6]K. L. Dahm, L. R. Jordan, J. Haase, and P. A. Dearnley, Surf. Coat. Technol. **109**, 413 (1998).
[7]H. J. Jureschke and R. Steinitz, J. Chem. Phys. **4**, 118 (1958).
[8]T. N. Oder, J. R. Williams, M. J. Bozack, V. Iyer, S. E. Mohney, and J. Crofton, J. Electron. Mater. **27**, 324 (1998).
[9]Y. Sakamaoto, M. Nose, T. Mae, E. Honbo, M. Zhou, and K. Nogi, Surf. Coat. Technol. **174**, 444 (2003).
[10]M. Zhou, M. Nose, Y. Makino, and K. Nogi, Thin Solid Films **344**, 234 (1999).
[11]M. Zhou, M. Nose, Y. Makino, and K. Nogi, Thin Solid Films **359**, 165 (2000).
[12]D. Goedde and G. S. Girolami, J. Am. Chem. Soc. **126**, 12230 (2004).
[13]W. E. J. Reid, J. M. Bish, and A. Brenner, J. Electrochem. Soc. **104**, 21 (1957).
[14]H. R. Hoekstra and J. J. Katz, J. Am. Chem. Soc. **71**, 2488 (1949).
[15]Growth reactor ⟨www.mse.uiuc.edu/faculty/abelson.html⟩
[16]T. Schwarz-Selinger, A. von Keudell, and W. Jacob, J. Vac. Sci. Technol. A **18**, 995 (2000).
[17]K. G. Tschersich and V. von Bonin, J. Appl. Phys. **84**, 4065 (1998).
[18]D. L. Chambers, K. A. Taylor, C. T. Wan, and A. J. Emrick, Surf. Coat. Technol. **41**, 315 (1990).