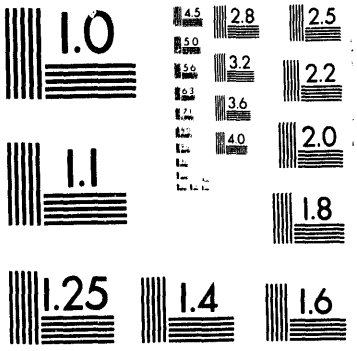
1.0
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

1 of 1

SAND93-4079C
Conf-931108--49

THE ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION OF TRANSITION METAL CARBIDES: THE USE OF HOMOLEPTIC ALKYLS

Matthew D. Healy,* David C. Smith,* Rodrigo R. Rubiano,** Robert W. Springer***
and John E. Parmeter****
*CST-3, MS-C346, Los Alamos National Laboratory, Los Alamos, NM, 87545
**Dept. of Nuclear Eng., Massachusetts Institute of Technology, Cambridge, MA, 02139
***MST-7, MS-E549, Los Alamos National Laboratory, Los Alamos, NM, 87545
****Dept. 1126, Sandia National Laboratories, Albuquerque, NM, 87105

ABSTRACT

The organometallic chemical vapor deposition (OMCVD) of transition metal carbides (M = Ti, Zr, Hf, and Cr) from tetraneopentyl-metal precursors has been carried out. Metal carbides can be deposited on Si, Al_2O_3, and stainless steel substrates from $M[CH_2C(CH_3)_3]_4$ at temperatures in the range of 300 to 750 °C and pressures from 10^{-2} to 10^{-4} Torr. Thin films have also been grown using a carrier gas (Ar, H_2). The effects of variation of the metal center, deposition conditions, and reactor design on the resulting material have been examined by SEM, XPS, XRD, ERD and AES. Hydrocarbon fragments generated in the deposition chamber have been studied by in-situ mass spectrometry. Complimentary studies examining the UHV surface decomposition of $Zr[CH_2C(CH_3)_3]_4$ have allowed for a better understanding of the mechanism leading to film growth.

INTRODUCTION

The interest in the use of organometallic complexes as precursors for the deposition of thin film materials has increased greatly over the last quarter century [1]. Over a century ago, Mond *et al.* [2] deposited Ni from $Ni(CO)_4$, although the modern use of organometallic complexes in deposition systems is often traced to Manasevit and co-workers [3] efforts in the late 1960's. Since that time, the scope and sophistication of the resulting technology has grown to encompass many materials (such as metals, semiconductors, insulators, and superconductors).

Our interest in the organometallic chemical vapor deposition (OMCVD) of materials stems from interests in materials that can withstand harsh chemical environments and elevated temperatures. The initial focus was on the OMCVD of group 4 carbides. Our choice of precursor complex was based on literature precedent, reports by Girolami *et al.* [4] describing the use of $Ti[CH_2C(CH_3)_3]_4$ in the low-temperature, low-pressure deposition of high-quality TiC. This prompted us to investigate the corresponding Zr system for ZrC deposition. There has been a long standing interest in this laboratory [5] in the deposition of ZrC, using $ZrCl_4$, H_2,

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

and hydrocarbons as precursors in a process hindered by the involatility of the metal halide, incorporation of halide into the resulting material, and the need to control multiple precursor streams. We believed that the use of an appropriate organometallic precursors would allow us to avoid all of the above problems; the complex $Zr[CH_2C(CH_3)_3]_4$, $ZrNp_4$, is significantly more volatile than $ZrCl_4$, contains no halide, except possibility as an impurity, and is a single-source precursor for the material. We were successful in depositing thin films of crystalline ZrC (as determined by XRD) but our materials contained both excess carbon (as determined by XPS and AES) and hydrogen (as determined by ERD) [6]. These inconsistencies with the previous work has lead us to reinvestigate the $TiNp_4$ system in our deposition reactor, as well as investigating the $HfNp_4$ system.

The ability to compare and contrast these systems in parallel has enabled us to develop a better understanding of the deposition parameters important to this system. Simultaneously, we have investigated [7] the $Cr[CH_2C(CH_3)_3]_4$ system, first reported by Rutherford *et al.* [8] and later by Maury *et al.* [9] as a poor precursor for the OMCVD of Cr_xC_y.

In this paper, we will discuss the similarities and differences of these systems and, in conjunction with surface analysis and mass spectral data, describe the complexities involved in understanding these systems.

EXPERIMENTAL

Complete experimental details have been presented elsewhere [6]. Modifications are noted herein. Depositions were conducted in a horizontal, hot-walled CVD reactor. The base pressure of the system is approximately 10^{-6} Torr. This is achieved with a 330 l/s turbomolecular pump. An in-line liquid nitrogen trap was placed between the deposition chamber and the pumping system except when mass spectra were taken. The system may also be modified to allow for the use of Ar or Ar/H_2 carrier gas.

Collection of the mass spectral data was performed under conditions nearly identical to those of an actual deposition. Si(100) substrates were mounted on a BN stage perpendicular to flow through the quartz reactor tube. The tube was heated such that the stage was maintained at 560-570 °C for each of the organometallic species. Multiple scans were taken for each precursor once it had reached steady state, and a long pump/bake out period was allowed between each new precursor. Mass spectra analysis during this pump/bake out period confirmed that no residual hydrocarbon was present. In addition, standards of neopentane, isobutylene, and neopentane/isobutylene mixtures were passed through the system both at room temperature and at 560-570 °C. Appropriate pressures were regulated by a leak valve placed before the ionization port of the quadrupole.

Depositions involving carrier gas were performed with a modified precursor holder that allowed for the introduction of one or two gas streams. When hydrogen was used, it was introduced just before the hot zone to avoid problems associated with the reaction of hydrogen

with the precursor complex. The system was purged with carrier gas for ~0.5 h after being evacuated to a pressure of 10^{-6} Torr. Depositions were run using a mechanical pump and the coated substrates were allowed to cool *in vacuo* at 10^{-6} Torr. We observed that oxygen contamination may be reduced via these precautions.

Experimental details for the surface studies are presented elsewhere [10].

RESULTS AND DISCUSSION

Within the class of homoleptic alkyl complexes available for OMCVD in the group 4 triad, one is limited to those without β-hydrogens that have sufficient volatility at deposition pressures. The tetramethyls are quite unstable through alternate mechanisms [11]. To this end, the neopentyl ligand is the simplest, non-ring hydrocarbon available. Several variations in the ligand can be envisioned, such as changing the quaternary carbon for a silicon (silylneopentyl) and changing the t-butyl group of the neopentyl for phenyl (benzyl). Other workers have investigated the use of silylneopentyl systems of titanium with mixed results [12]. To date, no reports of the deposition of MC from the tetrabenzyl complexes have appeared.

The use of neopentyl ligands however does present some difficulties. The complexes MNp_4 have a metal to carbon ratio of 1:20 and a metal to hydrogen ratio of 1:44. Unless a facile decomposition mechanism is present for these complexes, there is a very real possibility of carbon and hydrogen impurities being incorporated into the growing films. It is exactly the presence of excess carbon and hydrogen in the growing films that lead us to investigate the mechanism of decomposition of the neopentyl ligand in this deposition system. We have investigated this for $TiNp_4$, $ZrNp_4$, $HfNp_4$, and $CrNp_4$.

The results of deposition experiments for Ti, Zr, and Hf are presented in Table 1. Temperatures above 500 °C are required to obtain stable films that are crystalline. All films show some amount of residual carbon (we have as yet not obtained good standards for the metal carbides: therefore we have used literature sensitivity values.). Hydrogen contents are also quite high; under the correct conditions oxygen contents may be kept quite low (<2%). These results are consistent across a number of deposition runs.

The case for chromium is presented at the bottom of Table 1. These data are in striking contrast to those for the group 4 elements. Crystalline Cr_7C_3 may be grown at 570 °C and 10^{-4} Torr; films grown at 520 °C are amorphous [13]. These results are similar to other reports of the OMCVD of Cr_xC_y from various precursors [8, 14]. The amount of amorphous carbon present in the resulting films is far less than in the group 4 system (as determined by XPS), although the amorphous carbon does account for the discrepancy between the observed crystalline phase and the AES Cr:C ratio. The amount of hydrogen present is also significantly lower than those observed for the group 4 systems. The oxygen content of the films is at or below the detection limit of our XPS/AES experiment (approx. 2%).

These differing results for the group 4 and $CrNp_4$ deposition systems prompted us to hypothesize that a different mechanism was available for the decomposition of the $CrNp_4$, presumably influenced by the presence of a d^2 valance configuration, thus differentiating it from the d^0 group 4 system. This hypothesis was tested by examining the off gasses from the CVD reactor for the four metal complexes.

Table 1. Growth of Metal Carbide Thin Films from Tetraneopentyl Precursors.

Compound	P, Torr	T, °C	Growth rate[a]	Composition[b]	H content[c]
$TiNp_4$	10^{-4}	570	0.5	$Ti_{1.0}C_{2.6}O_{0.02}$	13 %
$ZrNp_4$	10^{-4}	570	1.0	$Zr_{1.0}C_{2.0}O_{0.05}$	15%
$HfNp_4$	10^{-4}	590	0.8	$Hf_{1.0}C_{1.4}O_{0.06}$	14%
$CrNp_4$	10^{-4}	570	0.15	$Cr_{1.0}C_{1.1}$[d]	2%

[a] μm/h; [b] determined from AES Depth Profile; [c] ERD; [d] O level at detection limit of inst.

Previous workers have reported that neopentane accounts for 93-97% of the effluent with small amounts of isobutylene, propene, 2,2,5,5-tetramethylhexane, and 2,2,5,5-tetramethylhex-3-ene for the deposition of TiC from $TiNp_4$ [4]. For the $CrNp_4$ system, neopentane, isobutylene, 2,2,5,5-tetramethylhex-3-ene, and propene were observed, but no percentages were reported [8]. Solution phase decomposition studies in d_6-benzene by Lappert *et al.* [15] were reported twenty years ago. Neopentane was the only observed product from each of the group 4 complexes, with stability increasing down the triad. Our results differ from these previous findings.

We find evidence for the formation of neopentane and isobutylene in all four metal systems, albeit in differing ratios [16]. To the level of detection of our system, we see no propene nor coupled products. However, we find evidence for significant quantities of methane in the Zr system, lesser amounts in the Hf and Cr systems, and very little in the titanium system. We note that while neopentane and isobutylene have a small m/e = 15 feature, there is no evidence for a m/e = 16 feature in the control experiments [17]. In addition, there is a significant C_5 peak only in the Ti system [18]. The nature of the C_5 species is not known at present, but, curiously, $TiNp_4$ also has the highest percentage of neopentane in the effluent. The films grown from $TiNp_4$ also have the largest amount of residual C, but similar amounts of hydrogen as in the films grown from $ZrNp_4$ and $HfNp_4$. The $CrNp_4$, which gave such a different film, gives a mass spectrum qualitatively similar to that obtained for $ZrNp_4$ and $HfNp_4$.

The mass spectral data provides some insight into the complexity of the deposition system. At this time, there is not a clear correlation between off-gas composition and the

carbide material that is deposited. To closely probe the decomposition chemistry involved in the deposition process, we have investigated the surface decomposition of $ZrNp_4$ in a UHV system on thin films of ZrC deposited *in situ* onto Ni foils [10a]. The films deposited in the UHV chamber had a C:Zr ratio of 3-5:1 rather than 2:1 observed for the OMCVD materials, no doubt a result of the lower precursor pressures. Multilayers of the $ZrNp_4$ absorbed on Ni foils were characterized. Though not directly relevant to the surface chemistry of the precursor, characterization of the multilayer state is of great importance in establishing that the precursor is being dosed cleanly onto the surfaces studied. The multilayer results provide convincing evidence that the $ZrNp_4$ precursor can be dosed onto a surface in the UHV system with minimal decomposition. The results of these studies are fully reported elsewhere [10a].

The monolayer decomposition takes place in two distinct steps, as determined by thermal desorption studies. First, near 410 K, the loss of higher hydrocarbon fragments is observed, most notably m/e = 57, 41, and 29. These features are assigned to the loss of neopentane (although the loss of molecular species cannot be rigorously excluded). The loss of significant amounts of isobutylene is not observed. Near 500 K, the loss of methane is observed. This involves the cleavage of carbon-carbon bonds, and indicates a more extensive decomposition of some of the neopentyl ligands after the initial desorption of hydrocarbons from the monolayer has opened additional surface sites. Furthermore, it is found that methane desorption predominates following very small submonolayer $ZrNp_4$ exposures, while desorption of the heavier hydrocarbon species is observed only at higher coverages. The observation of methane evolution in the UHV experiments suggested that the extensive decomposition of some neopentyl ligands leads to the incorporation of excess carbon in the films. We speculated that addition of hydrogen might aid in the hydrogenation process to remove larger hydrocarbon fragments from the growing surface. Preliminary results for the depositions in the presence of Ar and Ar/H_2 carrier gas are inconclusive.

CONCLUSIONS

We have successfully grown crystalline thin films of group 4 and group 6 carbides from homoleptic tetraneopentyl precursors. These films contain varying amounts of residual C, O, and H. Studies have also been carried out to determine if UHV and mass spectral studies could shed light on the decomposition mechanism leading to film growth. UHV studies clearly show that the decomposition of $ZrNp_4$ takes place in two distinct steps, leading to the liberation of neopentane and methane, respectively. Mass spectral studies confirm the presence of neopentane and methane, but further show the presence of significant amounts of isobutylene and (for Ti) an unexplained C_5 moiety. Compositional studies of the resulting thin films would suggest that the effluent mixture from $CrNp_4$ would differ significantly from $TiNp_4$, $ZrNp_4$, and $HfNp_4$. However, $TiNp_4$ was found to differ from $CrNp_4$, $ZrNp_4$, and $HfNp_4$. Furthermore, the presence of methane in the effluent, whereas indicating that carbon-carbon bond breaking is

occurring during the deposition, is not sufficient evidence of the mechanism of excess carbon incorporation in the thin films.

We continue to study these systems in order to refine our understanding of the growth of thin films from large organometallic precursors.

ACKNOWLEDGMENTS

The authors thank Norman E. Elliott (LANL, MST-7) for X-ray diffraction and SEM data, Kevin Hubbard (LANL, MST-7) for assistance with ERD, and Andrew Tyler (Harvard U.) for assistance with the mass spectral data. The work performed at LANL was supported by a LDRD grant. The work performed at Sandia National Laboratories was supported by the U.S. Department of Energy under contract DE-AC04-76DP00789. MDH is grateful to Los Alamos National Laboratory for a post-doctoral fellowship.

REFERENCES

1. a) A. Zinn, B. Niemer, and H.D. Kaesz, Adv. Mater. **4**, 375 (1992). b) F. Maury, Adv. Mater. **3**, 542 (1991).
2. L. Mond, C. Langer, and F. Quincke, J. Chem. Soc. **57**, 749 (1890).
3. H.M. Manasevit, J. Crystal Growth **55**, 1 (1981).
4. G.S. Girolami, J.A. Jensen, D.M. Pollina, W.S. Williams, A.E. Kaloyeros, and C.M. Alloca, J. Am. Chem. Soc. **109**, 1579 (1987).
5. C.M. Hollabaugh, L.A. Wahman, R.D. Reiswig, R.W. White, and P. Wagner, Nuclear Technology **35**, 527 (1977).
6. D.C. Smith, R.R. Rubiano, M.D. Healy, and R.W. Springer in Chemical Perspectives of Microelectronic Materials III, edited by C.R. Abernathy, C.W. Bates, Jr., D.A. Bohling, and W.S. Hobson (Mater. Res. Soc. Proc. **282**, Pittsburgh, PA, 1993) pp. 643-649.
7. M.D. Healy, D.C. Smith, R.R. Rubiano, N.E. Elliott, and R.W. Springer, Chem. Mater., submitted.
8. N.M. Rutherford, C.E. Larsen, and R.L. Jackson in Chemical Perspectives of Microelectronic Materials, edited by M.E. Gross, J.M. Jasinski, and J.T. Yates, Jr. (Mater. Res. Soc. Proc. **131**, Pittsburgh, PA, 1989) pp.439-445.
9. F. Muary and F. Ossola, Thin Solid Films **207**, 82 (1992).
10. a) J.E. Parmeter, D.C. Smith, and M.D. Healy, J. Vac. Sci. Technol., submitted. b) J.E. Parmeter, J. Phys. Chem. **97**, 11530 (1993).
11. P.J. Davidson, M.F. Lappert, and R. Pearce, Chem. Rev. **76**, 219 (1976).
12. T.J. Groshens, C.K. Lowe-Ma, R.C. Scher, and R.Z. Dalbey in Chemical Perspectives of Microelectronic Materials III, edited by C.R. Abernathy, C.W. Bates, Jr., D.A. Bohling, and W.S. Hobson (Mater. Res. Soc. Proc. **282**, Pittsburgh, PA, 1993) pp. 299-304.
13. Cr_7C_3 is a known phase. Reference is made to the JCPDS file number 36-1482.
14. F. Muary, F. Ossola, and F. Schuster, Surf. Coat. Technol. **54/55**, 204 (1992).
15. P.J. Davidson, M.F. Lappert, and R. Pearce, J. Organomet. Chem. **57**, 269 (1973).
16. Our observed neopentane/isobutylene ratios under CVD conditions are 2.03 (Ti); 0.99 (Zr); 0.69 (Hf); 0.76 (Cr). These values have been corrected for instrument sensitivity using isobutylene and neopentane. We believe that these values are correct to within 10%. Full details will be published in due course.
17. Because of the carbon isotopic ratio, the m/e = 15 feature is accompanied by a 1% relative intensity m/e = 16 feature. When methane is present, m/e = 16 is significantly more intense.
18. Neopentane does not have an observable C_5 fragment under our conditions.

DATE
FILMED
3/2/94

END