

Use of Tetraneopentylchromium as a Precursor for the Organometallic Chemical Vapor Deposition of Chromium Carbide: A Reinvestigation

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Thin films of chromium carbide have been grown by organometallic chemical vapor deposition (OMCVD) from tetraneopentylchromium ($\text{Cr}[\text{CH}_2\text{C}(\text{CH}_3)_3]_4$, CrNp_4). Deposition was performed in a hot wall, low pressure reactor at 520 and 570 °C and a pressure of 1.33×10^{-2} Pa (10^{-4} Torr). No carrier gas was used. The resulting films were characterized by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), X-ray diffraction (XRD), scanning electron microscopy (SEM), and elastic recoil detection (ERD). These data show that the films are of high quality, with very low oxygen content, and contain some residual amorphous carbon. Films grown at 570 °C are crystalline. The observed crystalline phase is Cr_7C_3 .

Introduction

Organometallic chemical vapor deposition (OMCVD) is presently experiencing considerable interest as a strategy for growing high-quality thin films of a variety of materials.¹ Although clearly minor in relation to the whole, papers dealing with the OMCVD of early transition metal carbides have enjoyed a long (beginning in 1967²) and of recent increasing interest in the literature. Germane to this recent interest is Girolami et al.'s 1987 paper on the OMCVD of TiC from tetraneopentyltitanium ($\text{Ti}[\text{CH}_2\text{C}(\text{CH}_3)_3]_4$, TiNp_4).³ That paper prompted us⁴ and others⁵ to investigate the use of neopentyl or modified neopentyl [i.e., $(\text{CH}_3)_3\text{SiCH}_2-$] metal species for the OMCVD of other metal carbides. The neopentyl systems are attractive because the metal is bonded only to carbon and because the species are blocked from decomposition via the usually facile β -hydride elimination reaction, are sufficiently volatile for use in OMCVD reactors, and are relatively easily synthesized and handled. We have found that standard Schlenk tube and drybox techniques coupled with modest care (storage at -40 °C and avoidance of light

as much as possible) leads to low oxygen contents in the films. Furthermore, we have found that seemingly minor transgressions in the deposition experiment can lead to greatly increased oxygen content in the films, despite very pure precursors. As we have reported elsewhere for the group IVB metal carbides,⁶ the resulting films may be unstable below a certain temperature and react with ambient atmosphere to increase the oxygen content in the films prior to characterization. We therefore took careful note of two recent reports on the OMCVD of chromium carbide from tetraneopentylchromium.⁷ Both papers reported successful deposition of films from the CrNp_4 precursor; however, both also reported very high oxygen contents in the films that *decreased* with increasing deposition temperature. In general terms, these results are not in conflict with ours, and we reasoned that the previous investigators had not gone high enough in temperature to deposit stable films with low oxygen contents. This paper describes our results on the OMCVD of chromium carbide from tetraneopentylchromium ($\text{Cr}[\text{CH}_2\text{C}(\text{CH}_3)_3]_4$, CrNp_4).

Experimental Section

CrNp_4 was synthesized according to literature methods⁸ and doubly sublimed at 50-55 °C *in vacuo* prior to use. The compound may be stored at low temperature (-40 °C) for a period of months.

Depositions were conducted in a horizontal, hot-walled CVD reactor at stage temperatures of 520 and 570 °C. The base

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pressure of the system is approximately 1.33×10^{-4} Pa (10^{-6} Torr). This is achieved with a 330 L/s turbomolecular pump. The pressure is monitored with an MKS electronic manometer, a Pirani gauge, or a cold cathode ionization gauge. An in-line liquid nitrogen trap was placed between the deposition chamber and the pumping system.

The Si(100) substrates were used as received. The substrates were mounted on a boron nitride (BN) stage with silver mounting paste and placed ~ 5 cm from the front of the furnace in an isothermal region. The stage rested on the bottom of the quartz tube with the substrates perpendicular to the flow through the reactor. The substrate temperature was monitored with a thermocouple embedded in the BN stage. The inlet side of the reactor was maintained at a temperature of 65–75 °C to avoid condensation of the precursor complex. The vessel that contained the organometallic complex was heated using an oil bath to ~ 60 °C to increase the vapor pressure of the compound and ensure a reasonable growth rate. Furthermore, the precursor was stirred to break up a thin crust that formed during the deposition. Typical deposition times were 2 h. The coated substrates were allowed to cool to room temperature *in vacuo* before being removed from the deposition system.

X-ray diffraction (XRD) studies were performed on a Rigaku RTP 300 rotating anode diffractometer with Cu irradiation or on a Philips APD 3720 with a silicon internal standard and raw data correction for instrumental error. The presence of crystalline Cr_7C_3 was confirmed by comparison to the X-ray powder diffraction patterns from the JCPDS for Cr_7C_3 , Cr_{23}C_6 , and Cr_3C_2 . Furthermore, least-squares unit-cell refinements were performed on a 570 °C sample on the corrected data from the latter diffractometer for both Cr_7C_3 and Cr_3C_2 . No solution could be obtained for Cr_3C_2 , whereas the final solution for Cr_7C_3 was in good agreement with the literature values.

Scanning electron micrographs were obtained in a Hitachi S520-LB scanning electron microscope. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were performed with a PHI Model 545 and Model 548 cylindrical mirror system. Electron beam conditions for AES were typically 5 keV and less than 1 μA total beam current in a spot size of 5 μm . Spectra were referenced to the Au $4f_{7/2}$ level at 83.95 eV from a gold standard film. X-ray irradiation for XPS was performed using an Mg source ($h\nu$ 1253.6 eV). Peak scans were obtained with a band pass of 25 eV and analyzer resolution of 1.6%. X-ray satellite peaks, X-ray line widths, and analyzer broadening were removed from the spectra using established von Cittert deconvolution procedures.⁹ AES depth profiling was performed using 3.5-keV Ar ions in a 2×2 mm² raster area. Elastic recoil detection (ERD) with a 2.0-MeV He⁺ beam was performed using the 3-MV tandem accelerator at the Ion Beam Materials Laboratory at Los Alamos National Laboratory. A Kapton foil was used as a standard with a known hydrogen content for ERD analysis.

Results and Discussion

Thin films of chromium carbide were grown from CrNp_4 at a stage temperature of 520 and 570 °C and a pressure of 1.33×10^{-2} Pa (10^{-4} Torr). Sublimation of the precursor is greatly helped by the use of a small stir bar, as an involatile overlayer forms on the precursor if it is not stirred. This overlayer accounts for a very small percentage of the material. The resulting films are gray in appearance, smooth, reflective, and uniform over the Si(100) substrate.

The salient features of the films grown at the two deposition temperatures are identical, with minor variations in composition, growth rate, and crystallinity. The following discussion of the characterization of these films concentrates only on the films grown at 570 °C. The

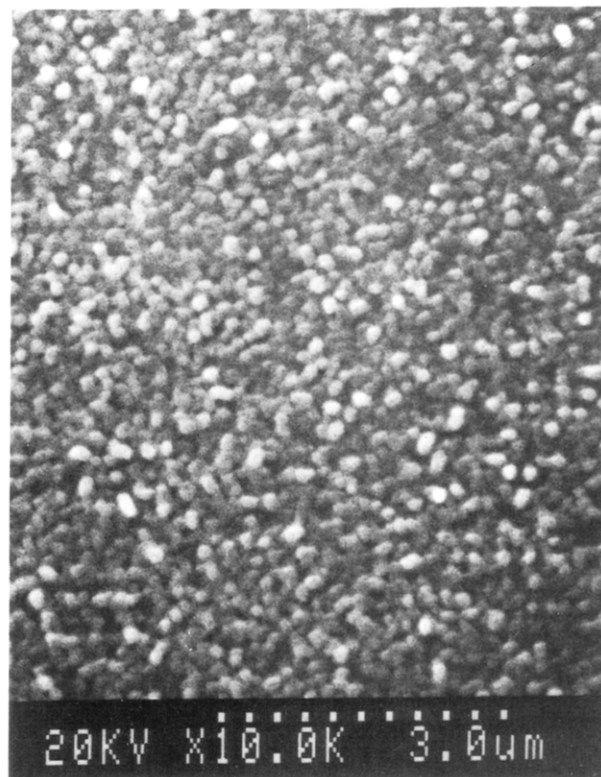


Figure 1. Scanning electron micrograph of the surface of a chromium carbide film deposited at 570 °C.

Table 1. Observed and Calculated 2θ Values and Unit-Cell Determinations from the Least-Squares Refinement of Cr_7C_3 for a Film Grown at 570 °C

<i>h k l</i>	2θ , lit. ^a	2θ , calc. ^b	2θ , obs. ^c	I, obs. ^c (lit. ^a)
1 5 0	39.188	39.195	39.2675	6(29)
1 1 2	42.545	42.547	42.7125	49(44)
1 5 1	44.166	44.174	44.2625	100(100) ^d
0 6 0	44.702	44.705	44.7775	12(13)
2 0 2	47.760	47.747	44.9025	4(5)
3 3 1	49.239	49.244	49.2900	15(12)
2 2 2	50.190	50.188	50.3625	25(27)
2 6 0	52.080	52.102	52.1800	14(19)
3 1 2	57.081	57.057	57.1025	2(3)
3 3 2	61.347	61.345	61.7525	15(3)
0 8 1	64.657	64.658	64.7250	20(7)
Unit-Cell Parameters:				
<i>a</i> , Å	7.0149	7.0189 ^e		
<i>b</i> , Å	12.1530	12.1368		
<i>c</i> , Å	4.5320	4.5137		
<i>V</i> , Å ³	386.3624	384.5079		

^a Reference is made to the JCPDS file number 36-1482, Cr_7C_3 . ^b 2θ values calculated from literature unit cell parameters. ^c Philips APD 3720 with θ compensating slit. ^d Fwhm = 0.26° (2θ). ^e Least-squares unit-cell refinement by NDSU version Fargo 87.08.01 using observed data.

differences are summarized following the discussion of the characterization of the films grown at 570 °C.

Scanning electron micrographs of the surface of the films show them to be quite smooth with a granular appearance at higher magnification (Figure 1). Surface features such as what we have observed previously for the Ti, Zr, and Hf systems are also present.^{4,6} Cross-sectional images show that the films are thin (0.3 μm) and exhibit a microcrystalline morphology. The growth rate at this temperature is low, ~ 0.15 $\mu\text{m}/\text{h}$. There is no evidence from these SEM data for columnar growth of the films. The films were found to give an X-ray diffraction pattern that corresponds to the known Cr_7C_3 phase. The diffraction experiment

(9) Deconvolution routines were written at Los Alamos National Laboratory.

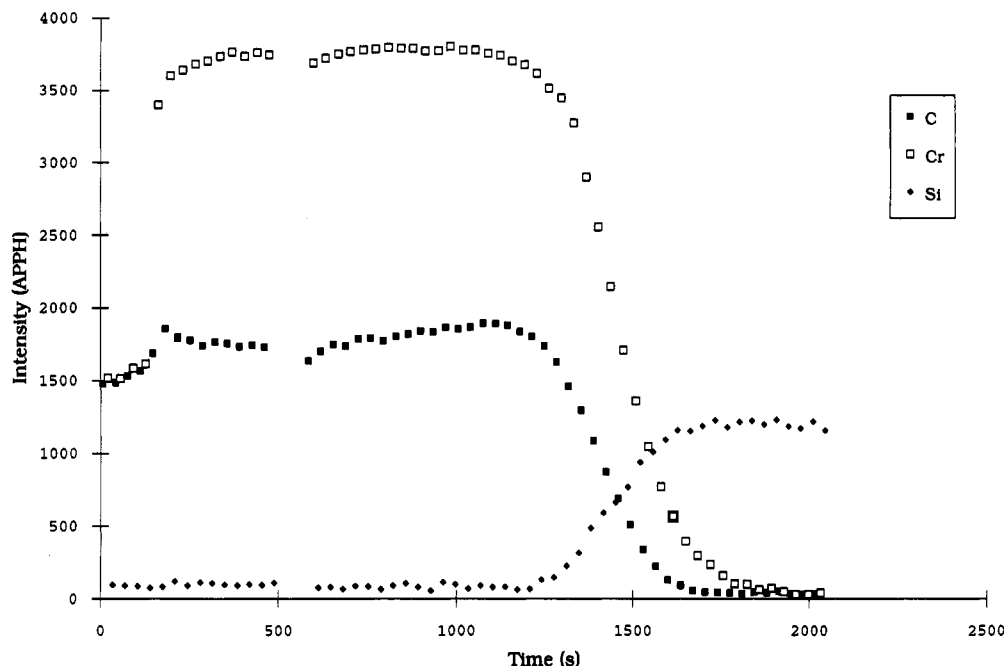


Figure 2. AES depth profile of the chromium carbide thin film deposited at 570 °C and 1.33×10^{-2} Pa (10^{-4} Torr).

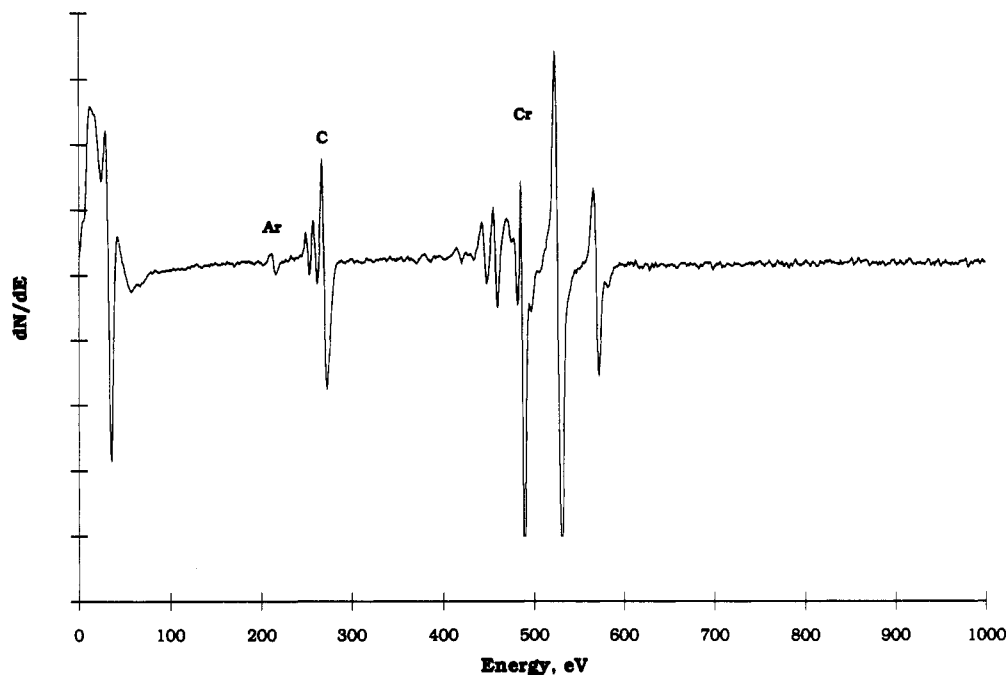


Figure 3. AE survey spectrum of the chromium carbide thin film deposited at 570 °C and 1.33×10^{-2} Pa (10^{-4} Torr) after sputtering.

results are presented in Table 1. Our measured intensities are in general agreement with the reported values. The fact that we see so many of the reported peaks and that the intensities generally match indicates there is no significant preferred orientation. Previous work on the OMCVD of chromium carbide from dicumene chromium¹⁰ also showed that the Cr_7C_3 phase is preferentially formed. In contrast, the diffraction patterns observed from the OMCVD of chromium carbide from $\text{CpCr}(\text{CO})_3\text{H}$ and $\text{Cr}(\text{N}^i\text{Pr}_2)_3$ most closely correlated to the Cr_3C_2 phase. With the group IVB neopentylmetal systems, we have observed that the resulting films have excess carbon (usually a 2:1 carbon to metal ratio) and X-ray diffraction patterns

corresponding to the MC phase.^{4,6} The chromium-to-carbon ratio that this phase (Cr_7C_3) implies is not supported by the Auger depth profile data (see below), and it is likely that this phase selectively crystallized from a sample that contains amorphous carbon.

Auger depth profile analysis of the thin films reveals that they are very uniform in composition (Figure 2) with a constant Cr:C ratio of approximately 0.9:1.0.¹¹ The small amount of oxygen present in the unspattered sample is easily removed by 5 min of sputtering. The oxygen content of the bulk of the film is not shown in the depth profile due to the low concentration of oxygen. Depth profiling for oxygen in chromium carbide is useful only for oxygen

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(11) Ratios are determined by applying literature sensitivity factors to the raw data. Sensitivity factors were determined from ref 12.

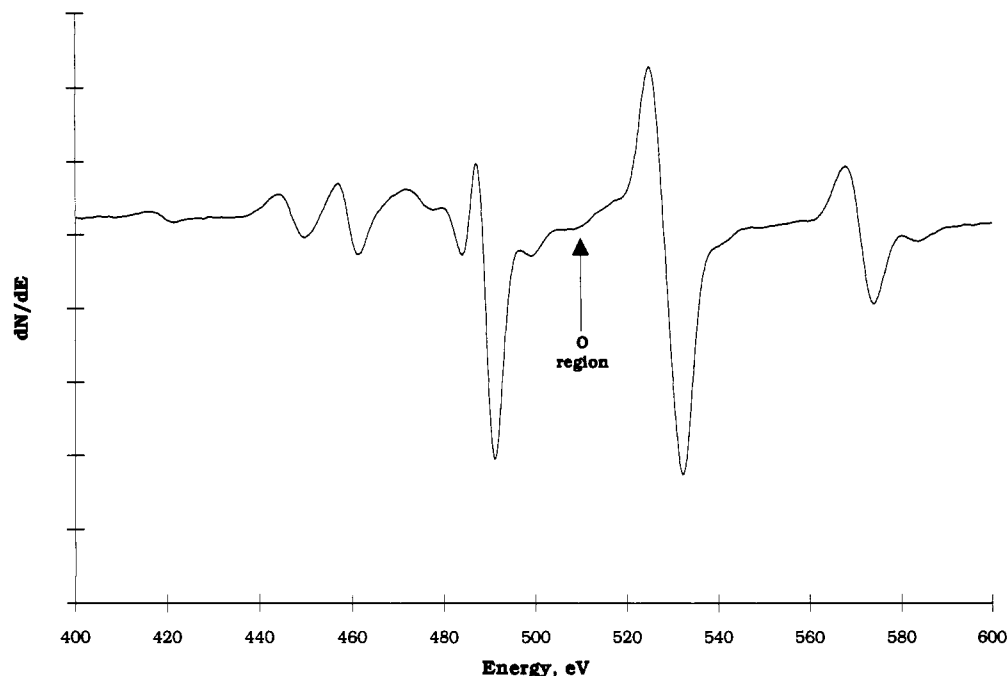


Figure 4. AE spectrum of the chromium region, 400–600 eV. Oxygen, if present, would give a signal at ~ 509 eV.

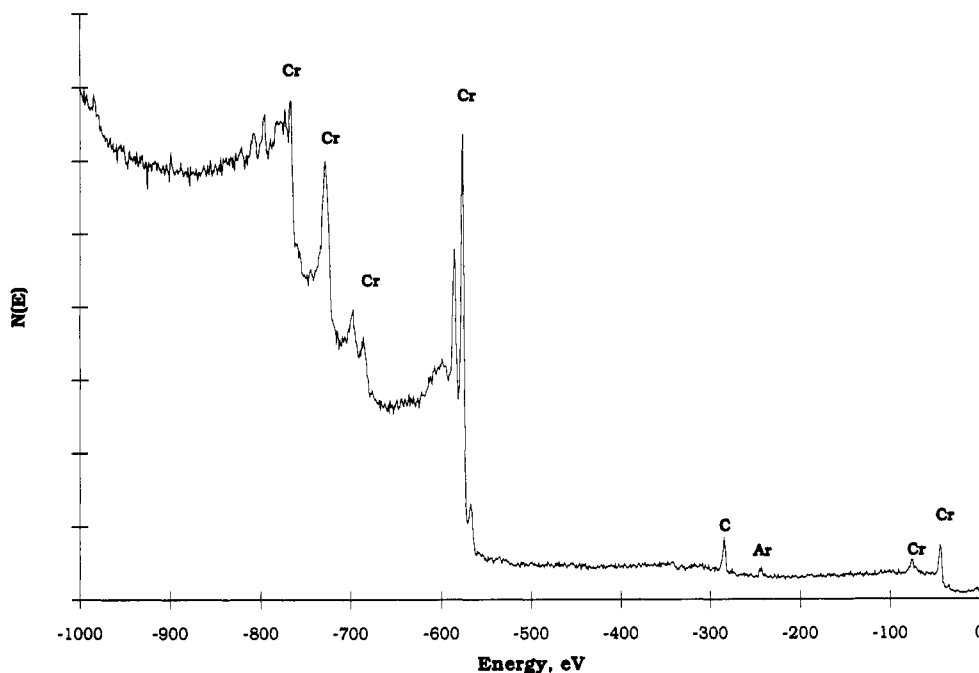


Figure 5. Survey spectrum of the chromium carbide thin film deposited at 570°C and 1.33×10^{-2} Pa (10^{-4} Torr) after sputtering.

contents $\sim 10\%$ and greater due to the overlap with the chromium signals. If profiling at a lower concentration is desired, more sophisticated treatment is required such as individual spectra storage and spectrum subtraction techniques. This additional sensitivity was not warranted in this work. We have therefore obtained an upper limit on the O content from XPS (see below). The Auger survey spectrum (Figure 3) shows a peak shape in the carbon region (250–280 eV) indicative of carbide.¹² Furthermore, the survey spectrum shows that the film contains chromium and carbon with no other discernible features (the peak at ~ 205 eV corresponds to Ar), the oxygen Auger

feature being obscured in the chromium region. Close examination of the Auger region of 400–600 eV (Figure 4) shows that very little if any O is present.

Survey XPS spectra of the films are consistent with what was observed in the AE spectra. The small oxygen content of the unspattered sample is again removed rapidly leaving a film that contains just Cr and C. A typical survey XPS spectrum of the spattered film is presented in Figure 5. The oxygen content of the material at both deposition temperatures is below our detection limit of the XPS technique. We estimate the upper limit of the oxygen present in the films to be 2.1–2.4%.¹³ Chromium XPS of

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(13) The upper limit was determined by analysis of the peak-to-peak noise in the oxygen peak region.

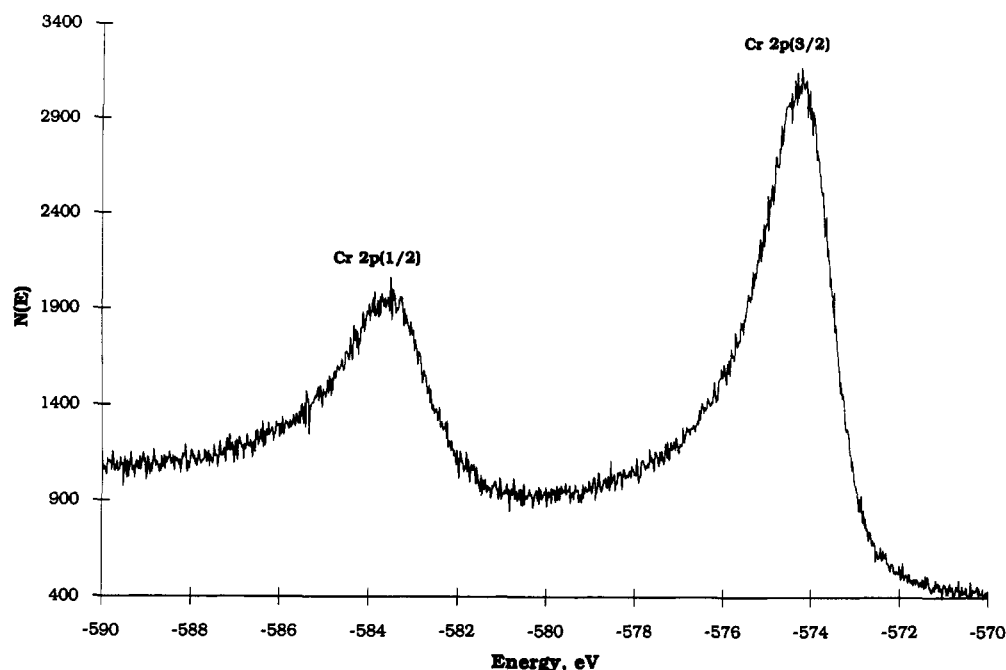


Figure 6. Chromium XP spectrum of the chromium carbide thin film deposited at 570 °C and 1.33×10^{-2} Pa (10^{-4} Torr) after sputtering.

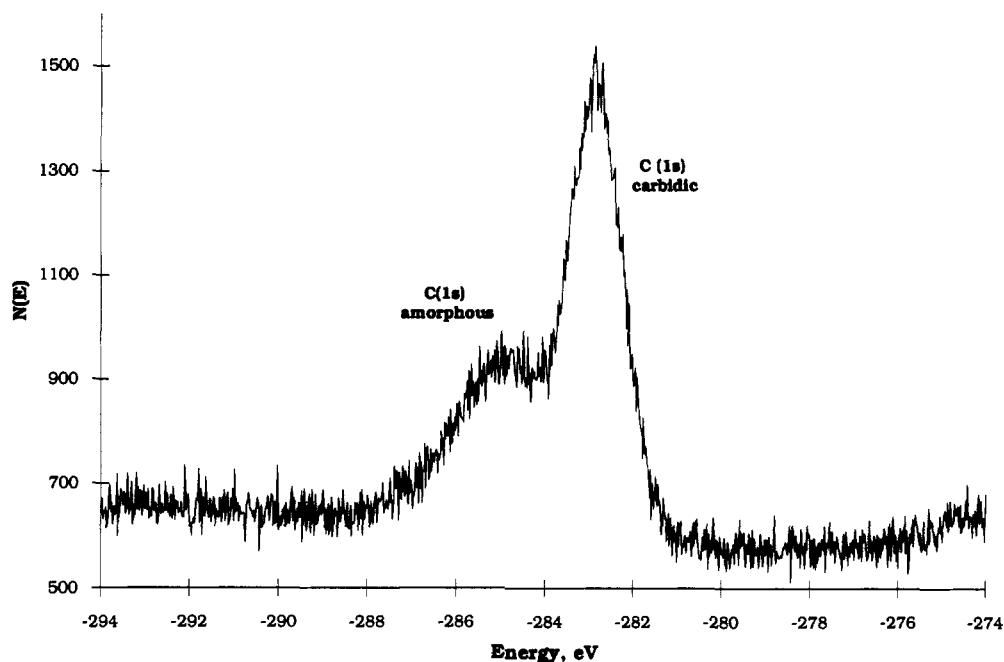


Figure 7. Carbon XP spectrum of the chromium carbide thin film deposited at 570 °C and 1.33×10^{-2} Pa (10^{-4} Torr) after sputtering.

the sputtered thin film (Figure 6) indicates that, in contrast to previous depositions with CrNp_4 , chromium oxide phases are not present. Peaks associated with the $\text{Cr } 2p_{1/2}$ and $\text{Cr } 2p_{3/2}$ levels are found at 583.6 and 574.2 eV, respectively. These data are consistent with the X-ray diffraction results; however, the presence of other chromium carbide phases (i.e., Cr_3C_2 and Cr_{23}C_6) and chromium metal cannot be excluded due to the coincidence of these Cr 2p peaks. The energy values for the $\text{Cr } 2p_{3/2}$ peak correspond well to those previously described for the thin films grown from CrNp_4 (574.4 eV),^{7b} $\text{CpCr}(\text{CO})_3\text{H}$ (574.2 eV),^{7a} and $\text{Cr}(\text{NiPr}_2)_3$ (574.2 eV).^{7a}

The carbon region of the XPS spectra shows two features (Figure 7).¹⁴ The peak to lower binding energy (282.8 eV) is assigned to the carbidic carbon in the sample. This

peak corresponds well to that observed for previous OMCVD CrC thin films, i.e., CrNp_4 (282.8 eV),^{7b} $\text{CpCr}(\text{CO})_3\text{H}$ (282.8 eV),^{7a} and $\text{Cr}(\text{NiPr}_2)_3$ (282.9 eV).^{7a} The peak to higher binding energy (284.8 eV) is assigned to amorphous carbon. In contrast to the TiC, ZrC, and HfC thin films grown from the tetraeneopentylmetal species, there is much less residual amorphous carbon present in the chromium carbide films. The ratio of chromium to carbon determined from the XP spectra is 1.3:1. Taking into account the presence of two carbon phases and subtracting out the contribution from the amorphous carbon, the ratio is 1.8:1. This is still somewhat smaller than the 2.3:1 ratio implied by the X-ray diffraction pattern.

(14) Carbon XP spectra were obtained by sputtering periodically (~every 20 min for 1 min) during a data collection of several hours.

In addition to the excess carbon in the deposited materials, we investigated the possibility that hydrogen is present in the thin films. Earlier efforts have observed residual hydrogen in materials deposited from organometallic precursors.^{4,6,15} Our previous efforts on the OMCVD of TiC, ZrC, and HfC revealed a considerable amount of hydrogen present in the films deposited from the tetra-n-pentyl metal precursors. For the zirconium system, up to 16% hydrogen was observed by elastic recoil detection. In this case however, we were able to detect only a very small amount of excess hydrogen (2.0–2.5%) in the films grown from CrNp₄. Why the hydrogen content of the films is so low with the chromium precursor is not clear to us at present. This observation is not, however, inconsistent with the observation that the amount of residual amorphous carbon in the films is greatly reduced in the chromium system compared to the Ti, Zr, and Hf systems.

The films grown at 520 °C show some differences with the films grown at 570 °C. Films grown at 520 °C show an increased growth rate (0.25 μm/h), slightly more carbon (AES depth profile gives Cr_{0.8}C_{1.0}), and are amorphous.

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The surface morphology, as shown by SEM, is identical, as are the hydrogen and oxygen contents.

Conclusions

We have been able to grow high-quality thin films of chromium carbide from CrNp₄ in an OMCVD reactor at 520 and 570 °C and 1.33 × 10⁻² Pa (10⁻⁴ Torr). The films grown at 570 °C are crystalline by X-ray, corresponding to the Cr₇C₃ phase. Auger depth profile data of the film show them to be very uniform, with a chromium to carbon ratio of 0.9:1.0.¹¹ The discrepancy in the X-ray and AES data is explained by the XPS data. These XPS data show some amount (~30%) of residual amorphous carbon to be present in the films. Surprisingly, very little hydrogen was detected by ERD.

These results contradict previous claims that CrNp₄ is a poor CVD precursor. In fact, in our hands it is an extremely good precursor. We note that experience has shown us that these temperamental systems may respond favorably under only certain conditions.

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