

Atmospheric-Pressure Chemical Vapor Deposition of Group IVb Metal Phosphide Thin Films from Tetrakisdimethylamidometal Complexes and Cyclohexylphosphine

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The dual-source atmospheric-pressure chemical vapor deposition of group IVb metal phosphide films from tetrakisdimethylamido(metal) and cyclohexylphosphine precursors is presented. Deposition took place at low temperatures (<500 °C), and nitrogen and carbon contamination of the films was negligible. The films had typical stoichiometric metal phosphide properties of high electrical conductivity, hardness, and chemical resistivity.

Introduction

Transition metal phosphides form an interesting series of compounds with several potential applications, for example the use of bulk powders for the catalysis of hydrodesulfurization and hydrodenitrogenation reactions,¹ as thin films in wear- and corrosion-resistant coatings,² and as diffusion barriers in semiconductor devices.³ However, the number of applications for transition metal phosphides is extremely limited compared to those of the corresponding nitrides, which have extensive technological applications,⁴ or the main group phosphides, InP and GaP, which have been exhaustively studied.⁵ Phosphides are generally classified by their stoichiometry as metal rich (M/P > 1), mono-phosphides (M/P = 1), or phosphorus rich (M/P < 1). The phosphorus-rich phases are typically thermally and chemically unstable, whereas the metal-rich and mono-phosphides are usually hard materials with high electrical conductivities.⁶ Titanium(III) phosphide (TiP) is one such material. It is a hard, refractory (dec < 1580 °C) metallic conductor, which shows good resistance to oxidation at elevated temperatures.⁷ It has been suggested for use as a barrier coating for Al–W metallization.⁸

Bulk TiP has been prepared by direct elemental combination⁹ and via the solid-state metathesis reaction

of TiI₄ with Na₃P.¹⁰ Crystalline powders have also been produced by the reduction of metal oxide/phosphate precursors in a flow of hydrogen.¹ Thin films of TiP have been deposited from the gas-phase reaction of TiCl₄ and PCl₃ under an argon/hydrogen atmosphere at temperatures between 850 and 1050 °C,⁷ and these high temperatures severely limit the choice of substrate. A thin film of TiP has also been formed by annealing titanium nitride under a phosphine atmosphere at 450 °C.⁸ Single-source CVD strategies to TiP were pioneered by Winter et al.¹¹ It was shown that the reaction of TiCl₄ with the primary phosphine, cyclohexylphosphine (Cy^{hex}PH₂), in hexanes produces an adduct [TiCl₄(Cy^{hex}PH₂)₂] which is a useful precursor for low pressure (LP) CVD. We extended this methodology to examine the reaction in solution of TiCl₄ with other primary organophosphines and also with secondary, tertiary, and chelating organophosphines.¹² A range of complexes of the type [TiCl₄(L)₂] (where L is a non-chelating organophosphine) and [TiCl₄(L')] (where L' is a chelating organophosphine) were formed. It was found that both primary and secondary phosphines produced complexes that were suitable precursors for LPCVD. An alternative route pursued by Watson et al. reported the synthesis of thin films of chromium phosphide via a low-pressure pyrolysis reaction of the single-source precursor [Cr(CO)₅(PH₃)].¹³ Recently, it has been shown that the gas-phase reaction of TiCl₄ with primary organophosphines¹⁴ or the tertiary phosphine (Me₃Si)₃P,¹⁵ provide superior routes to thin films of TiP via atmospheric-pressure (AP) CVD.

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Recent work on the deposition of group Vb metal phosphides demonstrated that the APCVD reaction of TaCl_5 with cyclohexylphosphine yielded thin films of the corresponding β -MP.¹⁶ However, when extending this methodology to the other group Vb metals¹⁷ it was concluded that reaction of VCl_4 with $\text{Cy}^{\text{hex}}\text{PH}_2$ required process temperatures higher than those of other transition metals examined.^{14,18} For the group IVb metals, although TiP is readily accessible from the metal(IV) chloride, the heavier congeners present a problem due to their involatility. Whereas TiCl_4 is a distillable liquid (bp 136 °C), ZrCl_4 and HfCl_4 are both solids with melting points around 300 °C and boiling points around 350 °C. The use of these solids in dual-source CVD for depositing metal phosphide films has been demonstrated in principle,¹⁹ however, the practical difficulties involved are not easily overcome.

The tetrakisdimethylamidometal complexes of group IVb are all volatile solids and it was proposed that the use of these complexes as metal precursors in the dual-source APCVD reaction with cyclohexylphosphine could provide facile routes to group IVb metal phosphides. Titanium, zirconium, and hafnium nitride films have been grown from the APCVD reaction of tetrakisdi-alkylamidometal complexes and ammonia at 200–450 °C.²⁰ The titanium, zirconium, and hafnium nitride films were analyzed as slightly nitrogen-rich TiN (N/Ti 1.05–1.15), Zr_3N_4 , and nitrogen-rich Hf_3N_4 (N/Hf 1.7 ± 0.1).²⁰ The films were largely free of carbon contamination, indicating that the NR_2 ligands are replaced (via amine elimination reactions) by NH_2 , NH , or N groups. Herein, we report the APCVD reaction of cyclohexylphosphine and tetrakisdimethylamidometal complexes of group IVb.

Experimental Section

APCVD experiments were conducted using SiCO-coated (SiCO is a barrier layer to stop diffusion of ions from the glass into the CVD produced film) float-glass substrates (90 mm \times 45 mm \times 4 mm) in a horizontal-bed cold-wall APCVD reactor. The glass was cleaned prior to use by washing with petroleum ether (40–60 °C) and propan-2-ol, and subsequent air-drying. A graphite block containing a Whatman cartridge heater was used to heat the glass substrate. The temperature of the substrate was monitored by a Pt–Rh thermocouple. Measurements indicated temperature gradients of less than 25 °C at 500 °C across the glass substrates. All gas handling lines, regulators, and flow valves were made of stainless steel and were of 1/4-in. internal diameter, except for the inlet to the mixing chamber and the exhaust line from the apparatus, which were 1/2-in. internal diameter. Nitrogen (99.99%), obtained from British Oxygen Company (BOC) and used directly from the cylinder, was preheated by passing along lengths of stainless steel tubing inserted inside a furnace. The temper-

atures of all the gas inlet lines were monitored by Pt–Rh thermocouples and Eurotherm heat controllers. Tetrakisdimethylamidotitanium [$\text{Ti}(\text{NMe}_2)_4$] was supplied by Epichem Ltd., and tetrakisdimethylamidozirconium [$\text{Zr}(\text{NMe}_2)_4$] and tetrakisdimethylamidohafnium [$\text{Hf}(\text{NMe}_2)_4$] were synthesized according to the literature.²¹ [$\text{Zr}(\text{NMe}_2)_4$] Calc: C, 35.96; H, 8.99; N, 20.97. Found: C, 35.71; H, 9.14; N, 20.93. [$\text{Hf}(\text{NMe}_2)_4$] ¹H NMR (C_6D_6): δ 2.98). Cyclohexylphosphine ($\geq 97\%$) was purchased from Strem Chemicals. The chemicals were placed into separate heated stainless steel bubblers, and the vapor generated was introduced into the gas streams by passing hot nitrogen gas through the bubblers. Gas flows were adjusted using suitable regulators and flow controllers. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. All of the apparatus was baked out with nitrogen at 150 °C for 60 min before deposition. Deposition experiments were conducted by heating the horizontal bed reactor and the bubbler to the required temperatures before diverting the nitrogen line through the bubbler and hence to the reactor. At the end of the deposition the bubbler-lines were closed and only nitrogen passed over the substrate. The glass substrate was allowed to cool with the graphite block to ca. 150 °C before it was removed. Coated substrates were handled and stored in air. The large coated-glass sample was broken up for subsequent analysis by X-ray photoelectron spectroscopy (XPS), energy dispersive analysis of X-rays (EDAX), wavelength dispersive analysis of X-rays (WDX), scanning electron microscopy (SEM), Raman, sheet resistance, glancing angle X-ray diffraction (XRD), and Scotch tape tests.

X-ray powder diffraction patterns were measured on a Siemens D5000 diffractometer using monochromated $\text{Cu K}\alpha_1$ radiation ($\lambda_1 = 1.5406 \text{ \AA}$) utilizing a position sensitive detector (PSD). The diffractometer was used in grazing incident geometry (1.5°). Data manipulation was performed using Bruker EVA software, and samples were indexed using Unit Cell and compared to database standards. EDAX/WDX was obtained on a Phillips XL30 ESEM (EDAX accelerating voltage 20 kV, WDX accelerating voltage 10 kV) using Oxford Instruments instrument control and Inca Wave analytical software. SEM was obtained on a Hitachi S570 (accelerating voltage 20 kV) using Oxford Instruments ISIS software. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. X-ray photoelectron spectra were recorded with a VG ESCALAB 220i XL instrument using focused (300 μm spot) monochromatic $\text{Al K}\alpha$ radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging, and the binding energies were referenced to an adventitious C 1s peak at 284.8 eV. Depth profile measurements were obtained using argon beam sputtering (etch voltage 5 kV). Electrical conductivity was determined by 4-probe measurement on glass substrates.

Deposition conditions are shown in Table 1. In all cases the total N_2 flow rate through the system was 2.4 L/min. Metal precursor/phosphine gas-phase molar ratios were calculated using vapor pressure data and nitrogen flow rates. For [$\text{Ti}(\text{NMe}_2)_4$] the metal bubbler was maintained at 150 °C with a flow rate of 0.4 L/min. To achieve a change in precursor gas-phase molar ratio the phosphine bubbler temperature was varied between 30 and 120 °C with the flow rate maintained at 0.4 L/min. No vapor pressure data were available for [$\text{Zr}(\text{NMe}_2)_4$] or [$\text{Hf}(\text{NMe}_2)_4$] so the metal bubbler temperature was arbitrarily set to 150 °C and the phosphine bubbler temperature was set to 100 °C with a N_2 flow rate of 0.4 L/min through each bubbler. In all cases the deposition run time was 1 min. The film thickness measurements were determined using SEM of a cross-section of the film/substrate taken from an identical point on each substrate (midpoint of substrate, 4 cm from leading edge), with the spread of results indicating the range obtained between different films. The EDAX/WDX

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Table 1. Experimental Deposition Conditions for the APCVD Reaction of $M(\text{NMe}_2)_4$ and $\text{Cy}^{\text{hex}}\text{PH}_2$

| metal precursor | metal precursor/phosphine gas-phase molar ratio | substrate temp. ($^{\circ}\text{C}$) | film thickness (nm) | EDAX/WDX film analysis (at. %) | | | |
|-----------------------------|---|--|---------------------|--------------------------------|------------------|-------------------|------|
| | | | | M | P | N | C |
| $\text{Ti}(\text{NMe}_2)_4$ | 1:5 | 550 | N/D ^a | | | - | |
| $\text{Ti}(\text{NMe}_2)_4$ | ^b | 500 | N/D ^c | 34.5 | 0.0 | 30.5 ^d | 35.0 |
| $\text{Ti}(\text{NMe}_2)_4$ | 1:5 | 500 | 220–250 | 45.8 | 47.1 | ^e | 7.1 |
| $\text{Ti}(\text{NMe}_2)_4$ | ^b | 450 | N/D ^c | 33.2 | 0.0 | 30.8 | 36.0 |
| $\text{Ti}(\text{NMe}_2)_4$ | 1:30 | 450 | 60–80 | 43.4 | 42.3 | ^e | 14.3 |
| $\text{Ti}(\text{NMe}_2)_4$ | 1:5 | 450 | 190–200 | 44.7 | 49.0 | ^e | 6.3 |
| $\text{Ti}(\text{NMe}_2)_4$ | 1:1 | 450 | 110–130 | 45.5 | 47.6 | ^e | 6.9 |
| $\text{Ti}(\text{NMe}_2)_4$ | 10:1 | 450 | 80–100 | 45.3 | 48.0 | ^e | 6.7 |
| $\text{Ti}(\text{NMe}_2)_4$ | 50:1 | 450 | 70–90 | 46.5 | 47.1 | ^e | 6.4 |
| $\text{Ti}(\text{NMe}_2)_4$ | ^b | 400 | N/D ^c | 33.8 | 0.0 | 31.3 | 37.1 |
| $\text{Ti}(\text{NMe}_2)_4$ | 1:5 | 400 | N/D ^f | 46.0 | 47.8 | ^e | 6.4 |
| $\text{Ti}(\text{NMe}_2)_4$ | 1:5 | 350 | no film | | | | |
| $\text{Zr}(\text{NMe}_2)_4$ | ^b | 450 | N/D ^c | 34.8 | 0.0 ^g | 29.7 | 35.5 |
| $\text{Zr}(\text{NMe}_2)_4$ | N/D ^h | 450 | 215–220 | 41.5 | 49.6 | 0.0 | 8.9 |
| $\text{Hf}(\text{NMe}_2)_4$ | ^b | 450 | N/D ^c | 15.6 | 0.0 | 38.3 | 46.1 |
| $\text{Hf}(\text{NMe}_2)_4$ | N/D ^h | 450 | 140–190 | 36.8 | 56.8 | 0.0 | 6.4 |

^a Not determined. Deposition on leading edge of substrate only. ^b Metal precursor only. ^c Not determined. ^d Ti line coincident with N line in EDAX spectrum, therefore quantification is approximate. ^e In WDX analysis Ti line is close to N line preventing accurate quantification but N at. % <3. ^f Too thin for measurement (<50 nm). ^g Zr line coincident with P line in EDAX spectrum, therefore P not actually analyzed but must be zero as no phosphine precursor used. ^h No metal precursor vapor pressure data available.

analysis shown is for a sample film produced using the appropriate conditions. EDAX analysis was used to analyze films deposited from the metal precursor alone but due to line overlap in the energy spectrum (P line is coincident with the Si line (from breakthrough to the underlying substrate); Zr line is coincident with both P line and Si line; N line overlaps with Ti line) WDX was used to analyze film deposited from reaction of the metal precursor with the phosphine. Unfortunately, even the use of WDX does not allow for accurate analysis of the N content in a Ti-containing film because the Ti line disturbs the baseline close to the N peak making quantification difficult. In all cases breakthrough to the underlying glass substrate was observed, making quantification of oxygen impossible.

Caution. It should be noted that the dual source APCVD reaction of $M(\text{NMe}_2)_4$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ could conceivably proceed through a PH_3 intermediate. PH_3 is extremely toxic and can combine explosively with air. Care should be taken to conduct all experiments behind a blast shield and to ventilate to a fume cupboard the exhaust gases from the reactor.

Results and Discussion

The results show that the use of $[\text{Ti}(\text{NMe}_2)_4]$ alone at a substrate temperature of 500 $^{\circ}\text{C}$ deposited a matte brown film, localized to the front third of the substrate, with approximate composition TiNC. Similar results were obtained at 450 and 400 $^{\circ}\text{C}$ using $[\text{Ti}(\text{NMe}_2)_4]$ alone, although with greater substrate coverage. These experiments are in good agreement with previous results for the use of $[\text{Ti}(\text{NMe}_2)_4]$ in APCVD (Ti 26 at. %, N 25 at. %, C 35 at. %, balance O at 500 $^{\circ}\text{C}$; Ti 22 at. %, N 29 at. %, C 32 at. %, balance O at 400 $^{\circ}\text{C}$).²² At a substrate temperature of 500 $^{\circ}\text{C}$ the reaction of $[\text{Ti}(\text{NMe}_2)_4]$ with excess $\text{Cy}^{\text{hex}}\text{PH}_2$ (1:5 metal/phosphine ratio) deposits highly reflective gold films. The films were between 220 and 250 nm thick, giving a growth rate of ~ 235 nm/min. WDX analysis of the film showed a metal/phosphorus ratio of 1:1, i.e., TiP, with approximately 7% carbon contamination but with less than 3% nitrogen contamination (limit of accuracy due to proximity of Ti line to N line in WDX spectrum). The reduction of carbon contamination in the films on

introduction of phosphine into the system is striking, from typically >35% for $[\text{Ti}(\text{NMe}_2)_4]$ alone to $\sim 6\%$ for $[\text{Ti}(\text{NMe}_2)_4]$ and phosphine. The reduction in nitrogen "contamination" is also dramatic, from $\sim 30\%$ of film composition to being undetectable above the background (less than 3 at. %). Similar results were obtained for the reaction of $[\text{Ti}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ in a 1:5 gas-phase molar ratio at 450 and 400 $^{\circ}\text{C}$, again showing a TiP stoichiometry with $\sim 6\%$ carbon contamination and less than 3% nitrogen. Cross-sectional SEM measurement of the film thickness showed that films deposited at 450 $^{\circ}\text{C}$ were between 190 and 200 nm thick (~ 195 nm/min growth rate) and those deposited at 400 $^{\circ}\text{C}$ were less than 50 nm thick (the limit of accurate measurement on the SEM instrument used). The reaction of $[\text{Ti}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ at 550 $^{\circ}\text{C}$ (1:5 gas phase molar ratio) deposited a film entirely localized at the leading edge of the substrate, and therefore unsuitable for analysis. Reaction of $[\text{Ti}(\text{NMe}_2)_4]$ and excess $\text{Cy}^{\text{hex}}\text{PH}_2$ (1:5 molar ratio) at 350 $^{\circ}\text{C}$ failed to deposit a film in the 1 min run time. The increase in film growth rate with increasing temperature for the reaction of $[\text{Ti}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ in a 1:5 gas-phase molar ratio suggests that film growth is controlled by the rate of reaction at the surface at the temperatures examined.

An investigation of the effect of precursor gas-phase molar ratio for the reaction of $[\text{Ti}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ was undertaken at 450 $^{\circ}\text{C}$. The film grown at 450 $^{\circ}\text{C}$ with a gas-phase precursor ratio of 1:5 was taken as the "baseline" for the study. Decreasing the amount of phosphine flowing through the reactor with constant molar flow of $[\text{Ti}(\text{NMe}_2)_4]$ decreased the rate of growth; 1:5 $[\text{Ti}(\text{NMe}_2)_4]$ /phosphine ratio 190–200 nm/min, 1:1 110–130 nm/min, 10:1 80–100 nm, and 50:1 70–90 nm/min. This decrease is to be expected, but the small change observed between the 1:1 ratio (110–130 nm/min) and 50:1 ratio (70–90 nm/min) is, perhaps, surprising. Interestingly, the film composition, determined using WDX, was almost invariant for films deposited with a $[\text{Ti}(\text{NMe}_2)_4]$ /phosphine ratio in the range 1:5–50:1, i.e., TiP + 6% carbon with less than 3% nitrogen.

The absence of change in the film composition and small change in film thickness with change in $[\text{Ti}(\text{NMe}_2)_4]/$ phosphine ratio (1:1–50:1) suggests that the active deposition species is at a low constant concentration compared to the precursor concentrations and again also indicates that film growth is surface reaction limited under these conditions. It also indicates that the exchange of N atoms for P atoms, in either the gas or condensed phase (or both), is extremely labile with comparatively low amounts of phosphine required to deposit a thin film of titanium phosphide. Increasing the amount of phosphine in the system, $[\text{Ti}(\text{NMe}_2)_4]/$ phosphine ratio from 1:5 to 1:30, had the effect of decreasing the film growth rate from 190 to 200 nm/min at a $[\text{Ti}(\text{NMe}_2)_4]/$ phosphine ratio of 1:5 to 60–80 nm/min at 1:30. Additionally, the level of carbon contamination in the film deposited with the 1:30 ratio more than doubled. The cause of the decreased growth rate and increased contamination is not known, however, an increase in carbon contamination was observed in TiN films deposited from $[\text{Ti}(\text{NMe}_2)_4]$ and NH_3 at higher deposition temperatures.²⁰ It was speculated that this was the result of intramolecular dimethylamido β -hydrogen activation occurring more readily at high temperatures and competing with inter- and intramolecular deposition chemistry. However, the increased carbon contamination from the 1:30 reaction of $[\text{Ti}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ is probably due to the presence of more phosphine and hence more carbon (cyclohexyl groups).

The decomposition of the metal precursor $[\text{Zr}(\text{NMe}_2)_4]$ alone in the CVD reactor deposited a dark film localized to the front third of the substrate. EDAX analysis over a number of locations indicated a composition consistent with that formed from the decomposition of $[\text{Ti}(\text{NMe}_2)_4]$, Zr 34.8%, N 29.7%, C 35.5%; i.e., ZrNC . The introduction of $\text{Cy}^{\text{hex}}\text{PH}_2$ into the system causes the deposition of a metallic-like, highly reflective silver film over the entire substrate with a growth rate of 215–220 nm/min. WDX analysis gave a film composition of slightly phosphorus rich ZrP with carbon contamination of ~9% but nitrogen contamination was below detection limits. Again, it was surprising that the nitrogen was removed from the system so effectively. These results were comparable to those obtained using $[\text{Ti}(\text{NMe}_2)_4]$.

Using $[\text{Hf}(\text{NMe}_2)_4]$ only, at a substrate temperature of 450 °C, caused the deposition of a dark film localized to the front third of the substrate. The film had a composition different from those deposited from $[\text{Ti}(\text{NMe}_2)_4]$ and $[\text{Zr}(\text{NMe}_2)_4]$, as determined by EDAX. The film composition was 15.6% Hf, 38.3% N, and 46.1% C, giving an approximate HfN_2C_3 stoichiometry. However, the use of $\text{Cy}^{\text{hex}}\text{PH}_2$ as a co-reactant reduced the levels of nitrogen and carbon in the deposited film to 0 and 6.4%, respectively. The film had a Hf_2P_3 stoichiometry as determined using EDAX which is different from the MP film stoichiometry found when using $[\text{Ti}(\text{NMe}_2)_4]$ or $[\text{Zr}(\text{NMe}_2)_4]$ with $\text{Cy}^{\text{hex}}\text{PH}_2$. There are no reports in the literature of a Hf_2P_3 phase, which may suggest that the film is a HfP phase with an overstoichiometry of phosphorus or perhaps a mixture of HfP and HfP_2 phases.

The surprising feature of all of the reactions examined was the ready inclusion of phosphorus in preference to

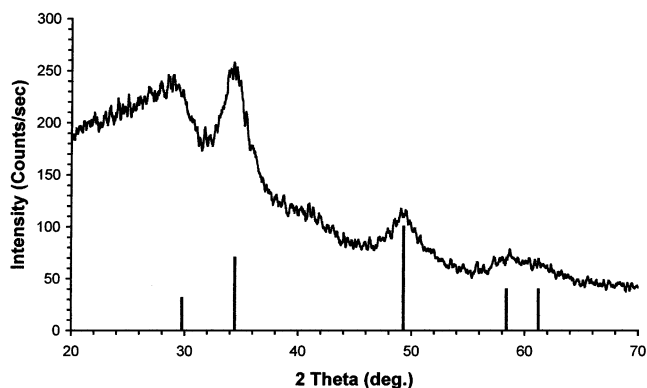


Figure 1. X-ray diffraction pattern of zirconium phosphide film.

nitrogen and the massive reduction in carbon contamination in the film even though the phosphorus precursor, $\text{Cy}^{\text{hex}}\text{PH}_2$, has carbon contained within it. Also, a change in film metal/phosphorus stoichiometry was observed between films deposited from $[\text{Ti}(\text{NMe}_2)_4]$ and $[\text{Zr}(\text{NMe}_2)_4]$ (M_1P_1) and the films deposited from $[\text{Hf}(\text{NMe}_2)_4]$ (M_2P_3). The reduction of carbon contamination in TiN deposited from $[\text{Ti}(\text{NMe}_2)_4]$ when using NH_3 as a co-reactant (contrast $\text{Cy}^{\text{hex}}\text{PH}_2$), and change in metal/nitrogen stoichiometry between $[\text{Ti}(\text{NMe}_2)_4]$ and $[\text{Hf}(\text{NMe}_2)_4]$ grown nitride films (with NH_3 co-reactant) have been observed previously.²⁰ Thus, the APCVD reaction of $[\text{M}(\text{NMe}_2)_4]$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) and NH_3 resulted in the formation of TiN, Zr_3N_4 , and nitrogen-rich Hf_3N_4 films. The formation of TiN suggests that a formal reduction from Ti(IV) in the precursor to Ti(III) in the TiN film has occurred. The mechanism for reduction is not known but it is thought to occur via Ti–N homolytic bond cleavage to produce a NR_2 or NH_2 radical and the Ti(III) center.²⁰ The fact that zirconium and hafnium did not show a reduction was thought to be due to the fact that the heavier metal $[\text{M}(\text{NR}_2)_4]$ compounds are more difficult to reduce. These results are in contrast to the formation of ZrP, involving a reduction from Zr(IV) in $[\text{Zr}(\text{NMe}_2)_4]$ to Zr(III) in the ZrP film, suggesting that the presence of phosphine aids the reduction.

To examine the films in more detail they were subjected to a variety of analysis techniques. Grazing angle X-ray diffraction indicated that all films deposited using $[\text{Ti}(\text{NMe}_2)_4]$, both with and without $\text{Cy}^{\text{hex}}\text{PH}_2$ co-reactant, were X-ray amorphous as deposited. The films deposited from $[\text{Hf}(\text{NMe}_2)_4]$ were also X-ray amorphous. The films deposited from $[\text{Zr}(\text{NMe}_2)_4]$ with no phosphine co-reactant were amorphous as deposited; however, the films deposited using $[\text{Zr}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C gave an X-ray diffraction pattern (Figure 1). The film indexed with unit cell $a = 3.71(4)$, $c = 12.8(6)$, which matches the literature values for h-ZrP.²³ Films deposited from the reaction of $[\text{Ti}(\text{NMe}_2)_4]$ or $[\text{Hf}(\text{NMe}_2)_4]$ with $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C, which were X-ray amorphous as deposited, were annealed in air at 600 °C for 18 h. After annealing the films remained amorphous.

Raman analysis was also utilized to examine the films. Films deposited from $[\text{Ti}(\text{NMe}_2)_4]$, $[\text{Zr}(\text{NMe}_2)_4]$, and $[\text{Hf}(\text{NMe}_2)_4]$ alone gave no Raman spectra. The

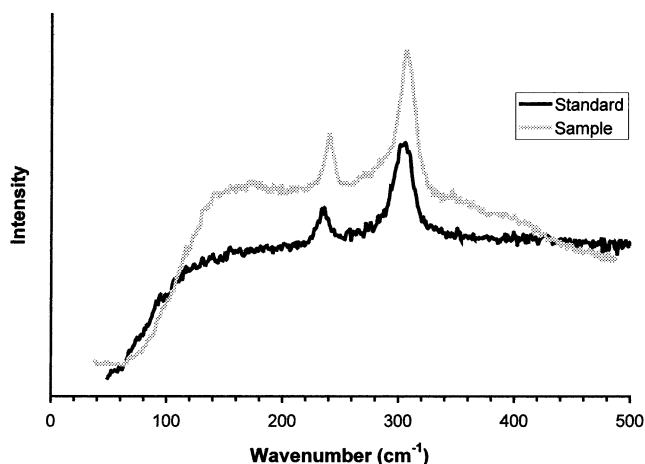


Figure 2. Raman spectra of h-TiP powder standard and titanium phosphide film.

films deposited from $[\text{Ti}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C gave identical Raman spectra, with characteristic bands at 235 and 305 cm^{-1} matching a TiP solid sample synthesized from TiCl_4 and Na_3P (Figure 2).²⁴ The films deposited from $[\text{Zr}(\text{NMe}_2)_4]$ or $[\text{Hf}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C gave no Raman patterns, or the pattern was so weak that it was not obviously differentiated from background noise.

XPS analysis of a film deposited from $[\text{Ti}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C with a metal/phosphorus gas phase molar ratio of 1:5 showed a relatively “clean” surface with very little “organic” (i.e., graphitic or adsorbed CO_2) carbon (C 1s 284.6 eV). The surface Ti 2p ionization was grotesquely misshapen with a peak maxima appearing at 458.6 eV. The major O 1s ionization was observed at 530.4 eV with a shoulder on the high energy side with approximate peak center at 532.4 eV, with these peaks being attributed to TiO_2 (lit. 530.6 eV) and PO_4^{3-} (lit. 532.4 eV), respectively.²⁵ The major P 2p ionization was centered at 128.5 eV, which is attributed to phosphide (lit. TiP 128.4 eV),²⁶ with a minor discrete peak at 133.5 eV (lit. PO_4^{3-} 133.4 eV)²⁷ in an approximate 90:10 ratio. A very small N 1s ionization was also present at 396.8 eV corresponding to nitride formation (lit. TiN 396.9 eV).²² The results indicate that the film surface is a mixture of TiP, TiO_2 , TiPO_4 , TiN, and C in an approximate 30:65:3:1:1 ratio (respectively), i.e., the surface of the film is principally oxide terminated with very little nitride and little carbon contamination. Argon etching into the film surface removed phosphate contamination and massively reduced oxide contamination. In the C 1s region of the spectrum 2 peaks were visible, one centered at 284.8 eV (graphitic) and one at 282.0 eV (carbide), although both were very minor.²¹ With an etch time of ~2 min, the film composition revealed using XPS was TiP, TiO_2 , TiN, TiC, and carbon in an 85:10:1:1:2 ratio. Further etching continued to decrease the levels of oxygen contamination in the film but the substrate was not reached, therefore it is difficult to know the precise level of oxide contamination in the

steady-state “bulk” film but between 5 and 10% is a reasonable estimate. Levels of nitride, carbide, and carbon contamination remained approximately constant in the etched layers. The XPS results support the Raman evidence that the deposited films are titanium phosphide (TiP). The oxidation of the film surface to oxide and phosphate is unsurprising and has been observed previously,^{12,14–18} but the low levels of graphite/carbide or nitride contamination are perhaps unexpected given the nature of the precursors used. XPS analysis of the film deposited from the reaction of $[\text{Ti}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C with a gas-phase metal/phosphorus molar ratio of 1:30 showed results almost identical to those obtained with a 1:5 ratio, although with slightly greater carbon contamination observed with an increase in the ratio of carbide relative to graphitic carbon. It is not thought that conclusions can be drawn about the origin of the carbide carbon because the total counts in the carbon peaks are so small that comparisons would be subject to a great deal of error.

XPS analysis of a film deposited from the reaction of $[\text{Zr}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C showed the film surface was phosphide (128.7 eV) contaminated with phosphate (133.2 eV) and oxide (529–535 eV). Argon ion etching for 30 s removed the P 2p ionization at 133.2 eV (phosphate) leaving only a singlet at 128.7 eV (phosphide), and the O 1s ionization narrowed and decreased in intensity. The Zr 3d region also clarified with the major ionization observed at $3d_{5/2}$ 179.2 eV being ascribed to a phosphide coordination. Further etching initially reduced the O 1s ionization, but after 2 min of etching a constant oxide contamination level was achieved. In the bulk film the composition was ZrP (92%) and ZrO_2 (8%) with no detectable carbon or nitrogen contamination. A depth profile of a typical XPS analysis is shown in Figure 3. This evidence, taken with the XRD data, shows that the reaction of $[\text{Zr}(\text{NMe}_2)_4]$ with $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C deposits crystalline films of ZrP with the only contaminant being in the form of oxide.

Analysis of a film deposited from the reaction of $[\text{Hf}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ at 450 °C was undertaken using XPS. Results were similar to the previous analyses with no N 1s ionization visible above background, and after etching through the surface no C 1s ionization was apparent. After etching, the only P 2p ionization present was at 128.2 eV, indicative of phosphide, with no ionization corresponding to phosphate present even on the film surface. There was no indication of a second phosphide ionization, which might be expected if the film was composed of two discrete phases (i.e., HfP and HfP_2) with the phosphide ionization at 128.2 eV being 3 eV wide, which is comparable to that observed for TiP and ZrP. An O 1s ionization occurred at 530.6 eV and decreased with subsequent etches until a steady concentration was achieved after 2 min of etching. The Hf 4f region displayed only one pair of peaks with $4f_{7/2}$ 14.8 eV, again with no evidence of a second ionization belonging to discrete phosphide phases. The bulk film composition was determined as hafnium phosphide (90%) contaminated with HfO_2 (10%), with no measurable carbon or nitrogen contamination.

The results show that the reaction of a tetrakis-dimethylamido compound of a group IVb metal with

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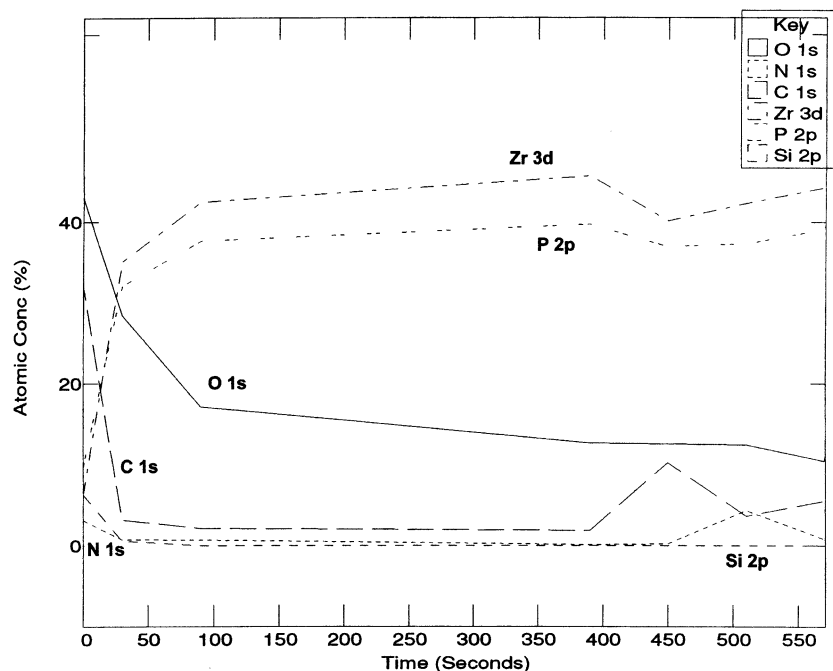


Figure 3. XPS depth profile of zirconium phosphide film.

$\text{Cy}^{\text{hex}}\text{PH}_2$ provides a readily accessible route to thin films of MP stoichiometry, with almost no carbon or nitrogen contamination. Physical tests showed that all films were adherent (passed Scotch tape test), although the $[\text{Hf}(\text{NMe}_2)_4]$ deposited film was easily abraded, with a paper towel normally sufficing. The $[\text{Ti}(\text{NMe}_2)_4]$ and $[\text{Zr}(\text{NMe}_2)_4]$ films were less easily abraded. Scratch tests showed that both the $[\text{Ti}(\text{NMe}_2)_4]$ and $[\text{Zr}(\text{NMe}_2)_4]$ films resisted scratching with a brass stylus but the $[\text{Zr}(\text{NMe}_2)_4]$ film failed when the stylus was changed to stainless steel. Resistivity measurements gave readings of 1000–2000 $\mu\Omega\text{cm}$ for the $[\text{Ti}(\text{NMe}_2)_4]$ deposited films comparing well with both bulk resistivity (3400 $\mu\Omega\text{cm}$)²⁸ and films deposited from TiCl_4 and $(\text{Me}_3\text{Si})_3\text{P}$ (3000 $\mu\Omega\text{cm}$).¹⁵ Films deposited from $[\text{Zr}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ had room-temperature resistivities of 2400–2800 $\mu\Omega\text{cm}$, whereas those deposited from $[\text{Hf}(\text{NMe}_2)_4]$ and $\text{Cy}^{\text{hex}}\text{PH}_2$ had higher resistivities of the order of 14000 $\mu\Omega\text{cm}$. Cooling the films down to -197°C caused the film resistivities to drop significantly in all cases, demonstrating that the films were behaving as metallic conductors over this temperature range. Subsequent testing of the films after standing in air over a period of six months showed no change in the film resistivities, indicating that film oxidation most likely took place immediately on removal from the reactor, and that the oxidation was self-limiting. Chemical tests showed that all of the films resisted immersion in common solvents (dichloromethane, ethanol, acetone, tetrahydrofuran, toluene, and water) indefinitely. The films deposited using $[\text{Hf}(\text{NMe}_2)_4]$ as the metal precursor were rapidly digested (~ 1 day) by concentrated (16 M) nitric acid and

concentrated (12 M) hydrochloric acid, and those deposited using $[\text{Ti}(\text{NMe}_2)_4]$ and $[\text{Zr}(\text{NMe}_2)_4]$ showed no deterioration in concentrated nitric (2 weeks immersion) but were both stripped in concentrated hydrochloric acid (~ 1 week). These results are comparable to transition metal phosphides deposited from metal chlorides.^{14–18} Water droplet contact angle measurements of films showed they were hydrophobic. The films were opaque to UV, visible, and near infrared radiation, but showed good reflection across these regions with slightly greater reflection observed toward the red/near infrared region. The films showed no photocatalytic activity toward the decomposition of stearic acid. These results are consistent with the deposition of TiP from TiCl_4 and various phosphines.^{14,15}

Conclusions

The results show that the use of $[\text{M}(\text{NMe}_2)_4]$ (where $\text{M} = \text{Ti}, \text{Zr},$ or Hf) in dual-source APCVD with $\text{Cy}^{\text{hex}}\text{PH}_2$ provides a readily accessible low-temperature route to MP phases. The evidence shows that MP phases deposited from $[\text{Ti}(\text{NMe}_2)_4]$ and $[\text{Zr}(\text{NMe}_2)_4]$ are partially crystalline hexagonal-MP, whereas films deposited from $[\text{Hf}(\text{NMe}_2)_4]$ are amorphous. Surprisingly, considering the nature of the precursors used, both nitrogen and carbon contamination of the films was minimal.

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