Chemical vapour deposition of Group Vb metal phosphide thin films

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The atmospheric pressure chemical vapour deposition (APCVD) reaction of VCl_4 and $VOCl_3$ with cyclohexylphosphine at substrate temperatures of 600 °C deposits thin films of amorphous vanadium phosphide. The films are black/gold, hard, chemically resistant and conductive. The APCVD reaction of MCl_5 (where M = Nb or Ta) with cyclohexylphosphine at 500 °C – 600 °C deposits films of crystalline β-MP and at 400 °C - 450 °C amorphous films of stoichiometry MP are formed. The MP films are metallic, conductive, adherent and chemically resistant.

1. Introduction

Transition metal phosphides form an interesting series of materials with a number of potential applications. Niobium(III) phosphide (NbP) is metallic, as hard as high carbon steel[1] and is resistant to attack by oxygen, sulfur dioxide and hydrogen sulfide up to 600 °C.[2] Tantalum(III) phosphide (TaP) is also metallic, very dense (~ 11 g/cm^3)[1] and even more chemically resistant than NbP.[2] It has been used as a diffusion barrier layer in semiconductor devices.[3] Similarly, vanadium(III) phosphide (VP) is a hard, metallic conductor.[1]

Bulk transition metal phosphides can be synthesised by direct elemental combination[4] or from reaction of the anhydrous metal halide with Na_3P.[5] Thin films of group Vb nitrides have been prepared from reaction of the metal chloride with nitrogen and hydrogen[6,7] or ammonia (with or without hydrogen).[8,9] Thin films of several transition metal phosphides have been synthesised from the reaction of metal chlorides with PCl_3 and hydrogen at temperatures above 850 °C.[2] The drawback with these methods are the high process temperatures required and the phosphorus analogue of ammonia, phosphine (PH_3), is a pyrophoric, extremely toxic gas. Winter et al have demonstrated a low pressure route (400 – 600 °C) to thin NbP films using a single-source precursor formed from the reaction of niobium(V) chloride and cyclohexylphosphine ($Cy^{hex}PH_2$) but this precursor showed significant decomposition at its sublimation temperature.[10] It has also been shown that the reaction of a metal chloride with a primary organophosphine (RPH_2) provides a readily accesible low temperature route to metal phosphides[11-14] and recently this has been demonstrated for the production of β-TaP from the reaction of $TaCl_5$ with $Cy^{hex}PH_2$.[15]

We have shown that TiP films can be made from the APCVD reaction of $TiCl_4$ and $Cy^{hex}PH_2$.[12] Here we report the first APCVD study of group Vb phosphides from the reaction of volatile halide precursors and $Cy^{hex}PH_2$. This paper also describes the effect of process conditions on the resultant films. We show that NbP and TaP films are metallic, hard and chemically resistant.

2. Experimental

Nitrogen (99.99%) was obtained by BOC and used as supplied. Coatings were obtained on SiCO coated float-glass (the SiCO is a barrier layer to stop diffusion of ions from the glass into the CVD produced film). APCVD experiments were conducted on 90 mm x 45 mm x 4 mm pieces of glass using a horizontal bed cold wall APCVD reactor. The glass was cleaned prior to use by washing with petroleum ether (40-60 °C), then propan-2-ol and subsequently dried in air. 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 that temperature gradients of less than 25 °C at 500 °C were noted across the glass substrates. The rig was designed so that two independent gas lines could be utilised. All gas handling lines, regulators and flow valves were made of stainless steel and were 1/4" internal diameter except for the inlet to the mixing chamber and the exhaust line from the apparatus that were 1/2" i.d. In these experiments three gas lines were used. Gases came directly from a cylinder and were preheated by passing along 2 m lengths of stainless steel tubing which was curled and inserted inside a tube furnace. The temperatures of all the gas inlet lines were monitored by Pt-Rh thermocouples and Eurotherm heat controllers. Vanadium(IV) chloride and vanadium(V) oxytrichloride (99%) were purchased from the Aldrich Chemical Co. and niobium(V) chloride (99+%), tantalum(V) chloride (99.9%), cyclohexylphosphine (≥ 97%), dicyclohexylphosphine (98%) and tricyclohexylphosphine (97%) from Strem Chemicals. The chemicals were used as supplied and placed into stainless steel bubblers. Tristrimethylsilylphosphine (($Me_3Si)_3P$) was synthesised according to a modified version of the literature procedure (^{31}P{H} NMR showed only a singlet at δ -251 ppm (($Me_3Si)_3P$) indicating purity > 98%) and was similarly placed into a stainless steel bubbler.[16] The bubblers were heated using a heating jacket and the vapour generated introduced into the gas streams by passing hot nitrogen gas through the bubblers. Streams of the precursors (highly diluted with nitrogen) were mixed by using concentric pipes of 1/4" and 1/2" diameter, the inner pipe being 3 cm shorter than the outer pipe. The concentric pipes were attached directly to the mixing chamber of the coater. 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 minutes before the runs. Suitable two-way and three way valves (rated to 200 °C) allowed the nitrogen lines to be diverted into or away from the bubbler. 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 XPS, EDAX,

SEM, Electron Probe Microanalysis (EPMA), transmission / reflectance and UV/VIS studies. Larger pieces of glass were used for sheet resistance, glancing angle X-ray powder, infrared, contact angle, photo-catalysis and Scotch tape tests.

X-ray powder diffraction patterns were measured on a Siemens D5000 diffractometer using monochromated CuK$_{\alpha 1}$ radiation (λ_1 = 1.5406 Å) utilising a Position Sensitive Detector (PSD). The diffractometer was used in glancing incident geometry (5°). Data manipulation was performed using Bruker EVA software and samples were indexed using Unit Cell and compared to database standards. SEM/EDAX was obtained on a Phillips XL30 ESEM using Oxford Instruments instrument control and Inca Wave analytical software. Electron Probe Micro-Analysis (EPMA) was obtained on a JEOL EMA and referenced against appropriate elemental standards. X-ray photoelectron spectra were recorded with a VG ESCALAB 220i XL instrument using focussed (300 µm spot) monochromatic 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 by using argon beam sputtering.

UV/VIS spectra were recorded in the range 200-1100 nm using a Helios double beam instrument. Reflectance spectra were recorded between 300 and 1200 nm by a Zeiss minature spectrometer. Measurements were standardised relative to a rhodium mirror. Electrical conductivity was determined by 4-probe measurement. Hardness scratch tests were conducted with felt pads, brass stylus and a stainless steel stylus.

Caution. It should be noted that the dual source APCVD reaction of MCl$_x$ and Cy^{hex}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.

3. Results

The conditions for the reaction of NbCl$_5$ and TaCl$_5$ with Cy^{hex}PH$_2$ are shown in Table 1. The metal halide/phosphine ratio shown is the gas phase ratio of moles MCl$_5$/moles Cy^{hex}PH$_2$ calculated from vapour pressure data and flow rates. However, the conditions under which the metal halide bubblers were operated, i.e. at temperatures below the solids melting point and with high N$_2$ flow rates, would cause non-equilibrium conditions. Therefore the values shown are an approximate guide to the gas phase molar ratio only. The conditions for the reaction of vanadium precursors (VCl$_4$ and VOCl$_3$) with various phosphines (Cy^{hex}PH$_2$, Cy^{hex}$_2$PH, Cy^{hex}$_3$P and (Me$_3$Si)$_3$P) are shown in Table 2. No vapour pressure data was available for Cy^{hex}$_2$PH, Cy^{hex}$_3$P and (Me$_3$Si)$_3$P. To ensure that the phosphine component was in excess the vanadium precursor bubbler temperature was lowered and run times extended to compensate for the resultant lower molar flow rates relative to reaction with Cy^{hex}PH$_2$.

3.1 APCVD of NbCl$_5$ and Cy^{hex}PH$_2$

The CVD reaction of NbCl$_5$ and Cy^{hex}PH$_2$ at 600 °C with a notional gas-phase Nb/P ratio of 1/400000 (Table 1) produced films that covered the entire substrate. The films were opaque and generally silver and highly reflective. However half-way from the front of the substrate, extending towards the back and localised in a central 'strip' the films were discoloured, appearing more matt and with a noticeable black colouration (Figure 1).
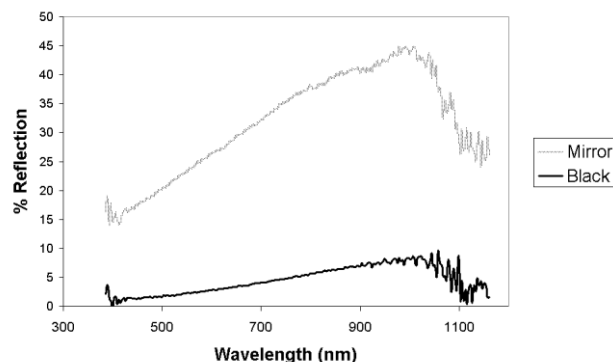

Fig. 1 Comparison of reflection spectra of mirror and black regions of β-NbP sample produced at 600 °C.

There was no noticeable change in composition in this region compared to the silver mirror region and no measurable increase in carbon contamination using EDAX. XRD showed the only crystalline phase present in each region was β-NbP with unit cell a = 3.30(2) Å, c = 11.6(2) Å (literature a = 3.325 Å, c = 11.38 Å).[17] It was concluded that the black strip is most likely due to very rapid film growth and is most probably due to aggregation of particulates in this region. EDAX indicated that the average metal/phsophorus composition across the whole surface was NbP$_{1.3}$. The high phosphorus reading may be misleading because breakthrough to the underlying glass substrate was observed and the silicon line from the glass is almost coincident with the phosphorus line in the EDAX spectrum causing difficulties in accurately quantifying these elements when they occur together. To examine this more closely an EPMA spectrum was obtained of the mirror portion of one film. The film was very slightly phosphorus rich (NbP$_{1.1}$) and even across the entire surface and had undetectable chlorine contamination.

XPS analysis of the mirror-like part of the film deposited at a substrate temperature of 600 °C revealed a surface with two phosphorus environments. The major P 2p ionisation was observed at 128.6 eV which is indicative of the formation of a transition metal phosphide[10,18] although a minor peak was observed at 133.8 eV, which has been attributed to phosphate[10]. The major surface Nb 3d$_{5/2}$ ionisation was observed at 203.2 eV identified previously as being associated with NbP[10]. A very minor Nb 3d$_{3/2}$ ionisation appeared at ~ 210 eV presumably from niobium oxide or niobium phosphate. A broad surface O 1s ionisation was centred on 530.6 eV suggesting both phosphate and oxide were present.[18] No peak for chlorine was observed. After argon ion etching (30 s) no peaks associated with oxygen or carbon were observed and the only P 2p and Nb 3d$_{5/2}$ ionisations remaining were at 128.6 eV and 203.2 eV respectively. This suggests that the oxygen contamination at the surface is a result of post-reaction oxidation and not as a result of the deposition process. The results also indicate considerably less oxygen contamination is present than that found using a single-source precursor to deposit NbP (combined C, O and Cl contamination ~ 10 at. %).[10] This may be as a result of the faster deposition rate and greater reactant flux associated with atmospheric pressure CVD than used in the comparable single-source low pressure CVD.[10]

Film thickness was measured by cleaving the film at the centre of the substrate and using SEM to view the film end-on. The films grown at 600 °C from NbCl$_5$ and Cy^{hex}PH$_2$ were determined to be between 250-300 nm thick (growth rate ~ 90 nm/min). The resistivity of the films varied between 2000 and 3000 µΩcm^{-1}. This compares well with the literature value for bulk NbP of 1700 µΩcm^{-1}.[1] Upon cooling to −197 °C the film exhibited a 50 % drop in resistivity. The values show

Table 1 CVD process conditions for the reaction of MCl$_5$ (where M = Nb or Ta) with Cy^{hex}PH$_2$

Metal halide precursor	Metal halide bubbler temp. (°C)	Metal halide bubbler N$_2$ flow rate (l/min)	Phosphine bubbler temp. (°C)	Phosphine bubbler N$_2$ flow rate (l/min)	Metal halide/ phosphine ratio (mol)	Substrate temp. (°C)	Run Time (min)	Thickness (nm)	EDAX (M/P ratio)	XRD
NbCl$_5$	150	2.0	120	0.3	1/400000	600	3	250-300	0.8	β-NbP
NbCl$_5$	150	2.0	120	0.3	1/400000	550	3	160-200	0.9	β-NbP
NbCl$_5$	150	2.0	120	0.3	1/400000	500	3	50-80	0.8	^{a}
NbCl$_5$	150	2.0	120	0.3	1/400000	450	3	^{b}	0.7	^{a}
NbCl$_5$	150	2.0	120	0.3	1/400000	400	3	^{c}	^{c}	^{c}
NbCl$_5$	190	2.0	100	0.3	1/180	550	3	^{d}	0.8	β-NbP
NbCl$_5$	190	2.0	80	0.3	1/50	550	3	^{d}	0.9	β-NbP
NbCl$_5$	190	2.0	60	0.3	1/12	550	3	^{d}	0.8	β-NbP
TaCl$_5$	160	2.0	130	0.1	1/50000	600	3	370-400	0.7	β-TaP
TaCl$_5$	160	2.0	130	0.1	1/50000	550	3	280-300	0.8	β-TaP
TaCl$_5$	160	2.0	130	0.1	1/50000	400	3	^{a}	^{a}	^{a}

^{a} Amorphous.
^{b} Film too thin for accurate measurement (less than 30 nm).
^{c} Film too thin for practical analysis (less than ~ 10 nm).
^{d} Not determined.

that the thin film NbP is a metallic conductor at the temperatures examined.

The films formed at 550 °C (Nb/P precursor gaseous molar ratio 1/400000) were opaque and entirely silver and mirror-like with no discolouration observed. The average composition observed using EDAX was NbP$_{1.1}$ and glancing angle XRD revealed the only crystalline phase was β-NbP (a = 3.32(3) Å, c = 11.7(3) Å).

The EPMA results (Figure 2) showed chlorine contamination was below detection limits and the film had an even composition across a distance of 5000 μm of NbP$_{1.1}$. The film thickness measured varied between 160 and 200 nm at the centre of the substrate (~ 60 nm/min growth rate) and room temperature film resistivities were 5000 – 6000 μΩcm^{-1}.
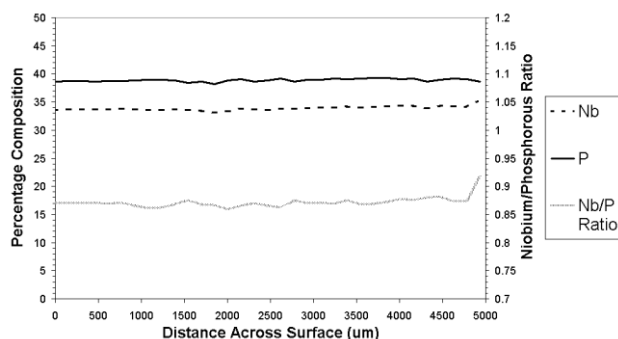

Fig. 2 EPMA composition of NbP film deposited at 550 °C.

Films formed at 500 °C (Nb/P precursor gaseous molar ratio 1/400000) were similarly silver and mirror-like although not completely opaque. The average niobium/phosphorus composition found by EDAX was NbP$_{1.3}$ with almost undetectable levels of chlorine contamination. The films were X-ray amorphous as deposited, between 50 and 80 nm thick at the centre of the substrate (~ 20 nm/min growth rate) and had resistivities of the order of 6000 μΩcm^{-1}.

Total coverage of the substrate also took place at a substrate temperature of 450 °C, with the films being noticeably thinner (optical transmission) although still highly reflective. Sheet resistance measurements showed that the films were metallic but film thickness measurement proved impossible by SEM. These films were also X-ray amorphous. At 400 °C deposition was observed but it was highly localised and too thin for practical analysis.

The change in growth rate with temperature (90 nm/min at 600 °C, 60 nm/min at 550 °C and 20 nm/min at 500 °C) and the complete surface coverage indicates that the reaction is surface rate limited under the conditions employed. Due to the glass substrates used (softening temperature ~ 600 °C) it was not possible to examine the temperautre required for mass transport limited growth to be exhibited under the precursor flow rates used.

An investigation of the effect of the precursor metal halide to cyclohexylphosphine ratio on the film properties was also undertaken. It was found that decreasing the moles of phosphine and increasing the moles of niobium(V) chloride (by altering the respective bubbler temperatures) had no discernible effect on the composition of the resultant film as determined by EDAX in the Nb/P gas phase molar ratio range 1/400000 – 1/12. Glancing angle XRD analysis of the resultant films indicated that all were β-NbP.

An experiment carried out at 550 °C with with identical precursor bubbler temperatures and flow rates to those shown in Table 1 but with a 1 minute run time deposited an extremely thin film with total substrate coverage. The film was too thin for practical analysis but was significantly less than 50 nm thick, as determined by cross sectional SEM. The growth rate at this temperature, determined from a 3 minute run time, would suggest a film thickness of 60 nm and therefore it seems likely that there is an induction period during which no significant film growth is observed.

SEM was used to examine the surface of the films formed from NbCl$_5$ and Cy^{hex}PH$_2$ deposited at 400 - 600°C and in all cases a crazy-paving like surface was observed, consistent with an island-growth formation mechanism. All the films were adherent to the substrate (Scotch tape test). Films deposited above 500 °C were hard, being resistant to abrasion by brass and steel but the films deposited at 500 °C and below were abraded by a steel stylus. The films were very chemically resistant, withstanding immersion in DCM, ether, toluene and concentrated (16 M) nitric acid with no optical deterioration over several weeks. Concentrated (12 M) hydrochloric acid dissolved the films over a period of a week.

3.2 APCVD of TaCl$_5$ and Cy^{hex}PH$_2$

Results for the reactions of TaCl$_5$ with Cy^{hex}PH$_2$ at various temperatures are summarised in Table 1. At 600 °C the films formed were localised to the front half of the substrate but no discolouration was observed as seen for niobium. The films were again highly reflective but appeared more golden in colour than

Table 2 CVD process conditions for the reaction of VCl_4 or $VOCl_3$ with R_xPH_{3-x} (where R = Cy[hex] and x = 1, 2 or 3 or R = SiMe$_3$ where x = 3)

Metal halide precursor	Phosphine	Metal halide bubbler temperature (°C)	Metal halide bubbler N$_2$ flow rate (l/min)	Phosphine bubbler temperature (°C)	Phosphine bubbler N$_2$ flow rate (l/min)	Metal halide/ phosphine ratio (mol)	Substrate temperature (°C)	Run time (min)	EDAX (V/P ratio)
VCl_4	Cy[hex]PH$_2$	100	0.3	130	0.3	1/5	600	1	0.8
VCl_4	Cy[hex]PH$_2$	100	0.3	130	0.3	1/5	500	1	No Film
VCl_4	Cy[hex]PH$_2$	100	0.3	130	0.3	1/5	400	1	No Film
VCl_4	Cy[hex]PH$_2$	100	0.3	130	0.3	1/5	300	1	No Film
VCl_4	Cy[hex]$_2$PH	60	0.3	200	1.6	a	600	2	No Film
VCl_4	Cy[hex]$_3$P	60	0.3	250	1.8	a	600	2	No Film
VCl_4	(Me$_3$Si)$_3$P	40	0.3	200	0.4	a	600	3	No Film
$VOCl_3$	Cy[hex]PH$_2$	40	0.3	100	0.3	1/8	600	2	0.7
$VOCl_3$	Cy[hex]PH$_2$	40	0.3	100	0.3	1/8	500	2	No Film
$VOCl_3$	(Me$_3$Si)$_3$P	30	0.2	200	0.4	a	600	2	0.6
$VOCl_3$	(Me$_3$Si)$_3$P	30	0.2	200	0.4	a	500	3	No Film

a Phosphine vapour pressures unknown.

the niobium films. The average Ta/P composition determined using EDAX was TaP$_{1.4}$ and no chlorine contamination was observed. Glancing angle XRD showed that the only crystalline phase present in a film was β-TaP.[16] The films were between 370 and 400 nm thick at the centre of the substrate (~ 130 nm/min growth rate) and had a room temperature resistivity of 3000 μΩcm[-1], almost identical to that of the NbP films. Cooling the films to –197 °C decreased the resistivity by more than 30 %, again indicating metallic-like behaviour at the temperatures examined.

The films formed at a substrate temperature of 550 °C showed total substrate coverage, were gold in reflection and had an average TaP$_{1.3}$ composition by EDAX with no chlorine contamination. A sample film indexed as β-TaP, as shown in Figure 3, with unit cell *a* = 3.33(3) Å, *c* = 11.6(2) Å (literature *a* = 3.330 Å, *c* = 11.39 Å).[17] The large, very broad absorbtion at ~ 25 – 40 °2θ is due to the amorphous glass substrate) The films were ~ 300 nm thick (~ 100 nm/min) with a room temperature resistivity of 6000 μΩcm[-1].
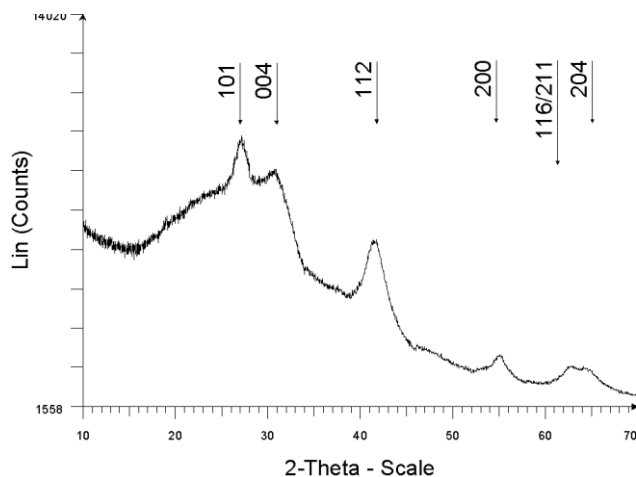

Fig. 3 XRD pattern of TaP film deposited at 550 °C.

At 400 °C a very thin film was deposited covering only a small part of the substrate. No meaningful analysis could be obtained from films deposited at this temperature.

XPS analysis of a film deposited at 550 °C showed that after etching through the surface contamination layer there was no detectable carbon or chlorine contamination. The P 2p ionisation was centred on a binding energy of 128.6 eV, which is indicative of a transition metal phosphide.[17] A small P 2p ionisation at

133.4 eV was also visible in the first two argon ion etched layers, indicative of oxygen contamination in the form of phosphate.[10] Also in the first two etched layers only an O 1s ionisation was observed at 530.8 eV but this was evidently formed from two separate peaks. The Ta 4f showed a set of major peaks with Ta 4f$_{7/2}$ at 21.8 eV and Ta 4f$_{5/2}$ 23.6 eV with minor peaks observed with Ta 4f$_{7/2}$ at 26.2 eV and Ta 4f$_{5/2}$ at 28.0 eV in the first two etched layers. In Ta$_2$O$_5$ the O 1s peak appears at 530.4 eV[19] and the Ta 4f$_{7/2}$ peak at 26.8 eV.[20] Again this indicates the oxygen contamination is as a result of post-reaction oxidation.

SEM of the films formed at substrate temperatures of 400 – 600 °C showed a crazy-paving like surface in all cases. All the films were adherent to the substrate and hard, resisting abrasion by brass and steel stylus. The films were extremely chemically resistant showing no change to common solvents or concentrated acids (nitric and hydrochloric) over several weeks immersion.

3.3 APCVD of VCl$_4$ and Cy[hex]PH$_2$

The conditions used for the reaction of VCl$_4$ with various phosphines are shown in Table 2. At 600 °C with a gas phase

VCl$_4$/Cy[hex]PH$_2$ mole ratio of 1/5 film deposition took place. The films were black with a gold sheen and substrate coverage was extremely limited (~ 4 cm^3) to the hottest (central) part of the substrate. Film formation was not entirely reproducible with some deposition experiments utilising identical conditions not yielding films. EPMA analysis of a sample film showed that the film had negligible chlorine contamination and an almost constant metal-rich surface composition of V$_{1.7}$P across a distance of 8000 μm.

XPS analysis of a film deposited at 600 °C showed that the surface had only one surface phosphorus environment, at 131.2 eV. This value is too high for VP (P 2p = 129.1 eV).[8] The surface vanadium environment V 2p$_{3/2}$ = 518.3 eV matches the value determined for vanadium in VOPO$_4$[21] but is too high for VO$_2$[22] or V$_2$O$_5$[23] (V 2p$_{3/2}$ ≈ 516 eV). The surface O 1s ionisation was broad and centred on 532 eV. The results suggest the surface is phosphate terminated, with little oxide or phosphide present. After etching the P 2p peak observed at 131.2 eV shifted to higher energy (P 2p = 132.6 eV) but almost disappeared with the major peak observed being P 2p = 129.2 eV, corresponding to VP.[18] After etching the vanadium peaks had poor shape with the major peak at V 2p$_{3/2}$ = 512.3 eV and minor peaks at V 2p$_{3/2}$ = 517.7 eV and V 2p$_{3/2}$ = 518.9 eV. The O 1s peak was extremely broad spanning 8 eV centred on O 1s = 531.4 eV. Although the P 2p and V 2p$_{3/2}$ ionisations are consistent with the formation of VP there are also vanadium ionisations consistent

with the formation of oxide and therefore it is thought the bulk composition of this sample is a composite of vanadium phosphide, vanadium oxide and vanadium phosphate.

At temperatures below 600 °C no deposition was observed under any conditions from reaction of VCl_4 and $Cy^{hex}PH_2$.

Measurement of film thickness for one of the films formed from $VCl_4/Cy^{hex}PH_2$, using end-on SEM, showed the film was 550 nm thick (550 nm/min). The film resistivity was 4000 $\mu\Omega cm^{-1}$, which is equivalent to the NbP and TaP films and comparable to that of the bulk powder (9700 $\mu\Omega cm^{-1}$).[1] SEM of the film surface showed a crazy-paving like morphology. The films were adherent to the substrate, were not abraded by a brass stylus but were scratched with a steel stylus. The films were not as chemically resistant as either the NbP or TaP films; although they survived immersion in common solvents (DCM, toluene, ether) they were rapidly stripped by both concentrated nitric and hydrochloric acids (1 day immersion).

3.4 APCVD of VCl_4 and Cy^{hex}_2PH, Cy^{hex}_3P or $(Me_3Si)_3P$

The reaction of VCl_4 with various other phosphines was also examined because of the limited success of the $VCl_4/Cy^{hex}PH_2$ system. It has been reported that the reaction of $TiCl_4$ with Cy^{hex}_2PH and Cy^{hex}_3P can yield films of TiP[24] and therefore the reaction of VCl_4 and these phosphines was examined. Under conditions similar to those used in Table 2 no deposition was observed over a series of experiments. The conditions shown are for the experiments undertaken which were most likely to yield thin films, i.e. highest substrate temperature and highest phosphine flow (phosphine bubbler temperature). However, despite this, no film could be obtained from the reaction of VCl_4 with Cy^{hex}_2PH or Cy^{hex}_3P.

The reaction of VCl_4 with $(Me_3Si)_3P$ was also examined; $(Me_3Si)_3P$ has been found to provide a route to high quality films of TiP from reaction with $TiCl_4$.[25] The reaction was speculated to be *via* elimination of trimethylsilylchloride (Eqn 1).

$$3TiCl_4 + 4(Me_3Si)_3P \longrightarrow 3TiP + 12Me_3SiCl + P \qquad [Eqn 1]$$

The conditions chosen were identical to those used successfully for the production of TiP from $TiCl_4$ and $(Me_3Si)_3P$. Despite this no deposition was observed and the values shown in Table 2 are for the highest substrate temperature and highest phosphine bubbler temperature used.

3.5 $VOCl_3 + Cy^{hex}PH_2$

Due to the difficulties encountered in reliably depositing thin films using VCl_4 a number of reactions utilising $VOCl_3$ were carried out. The reaction of $VOCl_3$ with $Cy^{hex}PH_2$ at 600 °C yielded black/gold films which were localised to a small (~ 2 cm^3) central (hottest) area of the substrate. EDAX measurements gave an average composition of $VP_{1.3}$. EPMA analysis of a sample film produced at 600 °C showed the film to be even across a surface distance of 5000 μm with an almost fixed composition of $V_{1.3}P$ whilst chlorine contamination was again negligible (< 1 at.%). The films were amorphous as determined by glancing angle XRD.

XPS analysis of a film deposited at 600 °C showed a phosphate terminated surface (V $2p_{3/2}$ 518.4 eV, P $2p$ 133.2 eV). Etching removed surface carbon and chlorine contamination. The bulk films, after argon ion etching, consisted of a phosphorus ionisation at P $2p$ = 129.2 eV and V $2p_{3/2}$ = 512.8 eV. These values match literature values for VP extremely well (P $2p$ 129.1 eV, V $2p_{3/2}$ 512.6 eV). A minor peak was observed for P $2p$ = 134.2 eV and the V $2p_{3/2}$ peak had a shoulder at 514.4 eV. An O $1s$ peak at 531.2 eV was observed in all levels but decreased significantly with etching. These data are interpreted as being due to a bulk composition of VP, oxidised to phosphate at the surface with some minor oxide contamination present. Due to the decreasing oxide contamination with etching it is thought the oxide is present through post-reaction oxidation as opposed to being due to the vanadium bound oxygen not being removed during the CVD process. End-on SEM showed that a sample film was 750 nm thick and resistivity measurements gave a value of 2000 $\mu\Omega cm^{-1}$. The films were rapidly digested by concentrated acids but were resistant to common solvents.

At temperatures below 600 °C no deposition was observed from reaction of $VOCl_3$ and $Cy^{hex}PH_2$.

3.6 $VOCl_3 + (Me_3Si)_3P$

The reaction of $VOCl_3$ with $(Me_3Si)_3P$ was also examined. The primary problem envisaged with the use of $VOCl_3$ with $Cy^{hex}PH_2$ was the lack of an obvious elimination pathway for the vanadium bound oxygen. It was thought that the use of tristrimethylsilylphosphine might allow elimination through the formation of a strong silicon-oxygen bond. In reactions between $VOCl_3$ and $(Me_3Si)_3P$ at substrate temperatures of 600 °C very thin (relative to the reaction between $VOCl_3$ and $Cy^{hex}PH_2$) black/gold films with limited coverage (~ 1 cm^3) were deposited. EPMA analysis of a sample showed the film to be much less even than that observed in previous samples, with the vanadium and phosphorus atomic percentages changing dramatically between analysis points. A small amount of chlorine contamination was observed in these samples (~ 1–2 at.%). The $V_{1.4}P$ although some variation was observed across the surface. No XPS analysis was attempted. The films were too thin to be able to determine the thickness using end-on SEM. Film resistivity measurement showed the films were metallic conductors. Chemical resistance of the films was equivalent to VP films deposited using $Cy^{hex}PH_2$.

No films were deposited from the reaction of $VOCl_3$ and $(SiMe_3)_3P$ at substrate temperatures below 600 °C.

4. Discussion

The APCVD reaction of MCl_5 (where M = Nb, Ta) with $Cy^{hex}PH_2$ deposits thin films of crystalline β-MP at substrate temperatures of 550 °C and above. At substrate temperatures of 400 °C and above deposition of amorphous metal phosphide films is observed. Changing the gas phase metal/phosphorus molar ratio had no discernible effect on the film composition or microstructure. The films were metallic and chemically resistant. The films had chlorine contamination below the detection limit of the analysis techniques used (< 1 at.%), indicating that the use of $Cy^{yhex}PH_2$ provides a facile elimination route for the metal-bound halide. Oxygen contamination was surface limited showing that it was as a result of post-reaction oxidation. The phosphide was oxidised to phosphate and oxide and it may be this that gives the thin films their excellent chemical resistance. It should be noted that the surface oxidation effectively forms a passivation layer and oxidation does not proceed beyond the first few atomic layers.

The APCVD reaction of VCl_4 with $Cy^{hex}PH_2$ deposited films of vanadium phosphide at temperatures of 600 °C. However the reaction did not reliably produce films. Initially it was thought that this may have been related to the temperature of reaction and also very rapid pre-reaction of the precursors. When deposition took place it was observed in the centre part of the substrate, an area which was found to be up to 25 °C hotter than the edges of the substrate. The reactor used is limited for use at 600 °C (the glass substrates begin to soften above this temperature) and therefore no higher temperature runs were attempted. However, another causal factor is thought to be the quality of the VCl_4 used for reaction. When deposition was

observed, repeat experiments utilising identical conditions, carried out immediately after an initial deposition reaction would also yield films. If the bubbler was not recharged for several days, or if a new batch of VCl_4 was used to recharge the bubbler the same conditions would often not yield films.

Observations made during the APCVD reaction of VCl_4 and $Cy^{hex}PH_2$ showed a thick purple smoke was produced in the bypass exhaust. Solution phase experiments in which VCl_4 and $Cy^{hex}PH_2$ were mixed yielded a purple solid but analysis showed that this was not an adduct of the type formed between the reaction of $TiCl_4$ and $Cy^{hex}PH_2$.[26] Low pressure CVD experiments using the solution-phase produced purple-solid showed no deposition up to 550 °C and it was concluded that it was not a suitable single-source precursor for low temperature thin film formation. This again may indicate that the temperature required to deposit films of vanadium phosphide from the product of reaction between VCl_4 and $Cy^{hex}PH_2$ is greater than seen for the reaction between $TiCl_4$ and $Cy^{hex}PH_2$.[12]

The difference between the film composition determined by EDAX and EPMA analysis has been attributed to the phosphorus and silicon lines being almost coincident in the EDAX spectrum. A further observation shows that the composition, as determined using EPMA, changes from slightly phosphorus rich ($NbP_{1.1}$) to metal rich ($V_{1.7}P$). This could be interpreted as being due to a difference in phase, i.e. NbP compared to V_3P_2 (or mixture of VP and V_2P). However this difference is ascribed to different levels of oxidation in the deposited films. In the films deposited with $NbP_{1.1}$ almost no oxidation was detected using XPS, and the oxidation present was extremely surface limited. In the films with a metal-rich stoichiometry ($V_{1.3}P$ and above) oxidation on the surface was severe and although decreased after etching was still present in the bulk as determined using XPS. This means that in the 'VP' film the EPMA result is a composite of, say, VP + VO_x which would increase the metal/phosphorus ratio observed. Interestingly less oxygen contamination was observed in the VP film deposited from $VOCl_3$ and $Cy^{hex}PH_2$ than in the film deposited from VCl_4 and $Cy^{hex}PH_2$.

From the XPS results the order of oxidation observed was β-NbP≈β-TaP<<VP. Both the NbP and TaP showed extremely surface limited oxidation whereas the VP showed much more extensive contamination extending further down into the film. This result is consistent with the findings of Ripley on bulk powders[1] and Motojima on films of metal phosphides.[2]

5. Conclusion

In conclusion this paper reports straight forward routes to Group Vb MP coatings. The reaction of MCl_5 (where M = Nb or Ta) with $Cy^{hex}PH_2$ provides a facile route to crystalline films of β-MP at temperatures of 550 °C and above. The reaction of VCl_4 and $VOCl_3$ with R_xPH_{3-x} (where R = Cy^{hex} and x = 1, 2 or 3 or R = Me_3Si and x = 3) deposits highly localised films of amorphous vanadium phosphide at 600 °C. The films are highly reflective and stable to a wide range of chemical reagents. The oxidation of the NbP and TaP films are surface limited (no change after 6 months storage in air). In all of the systems studied the rate of deposition was temperature dependent. This, coupled with the good film coverage of NbP and TaP, indicates a surface-reaction rate controlled CVD process.

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7. References

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