Chemical vapour deposition of titanium chalcogenides and pnictides and tungsten oxide thin films†

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This perspective article focuses on the formation of titanium chalcogenides and pnictides and tungsten oxides by chemical vapour deposition. Attention is focused on the role of the precursor and on the different microstructures that can be produced under different conditions.

1. Introduction

Chemical vapour deposition (CVD) is a versatile technique used to lay down thin films on the nanometre and micron scale. The technique involves transport of one or more precursor chemicals in the gas phase to a substrate, whereupon a chemical reaction occurs, resulting in the deposition of a film of solid material on the substrate. Our group has investigated the deposition of binary transition metal compounds by CVD, with a focus on developing films with useful functional properties. This article reviews that work, and discusses the pertinent issues in precursor design.

1.1 CVD techniques and apparatus

CVD is an umbrella term that encompasses a number of techniques, which are generally defined by the type of precursor used, the method of transporting the precursor and the method of initiating the chemical reaction. The name of the CVD technique is usually taken from one of these three factors, thus the names plasma enhanced CVD and photo assisted CVD describe the methods of initiating the reaction, low pressure CVD and aerosol assisted CVD describe methods of precursor transport, and metal organic CVD describes the type of precursor used.[1] What this practice sometimes obscures is that many different apparatus set-ups can be used, and that this can have as much influence on the end result as the three factors mentioned above. For example, CVD might be carried out with a hot-wall or cold-wall reactor, with a horizontal or vertical, rotating or stationary substrate, leading to very different results in each case. In addition, a further division can be made into single source CVD, where a single precursor chemical is used, and dual (or multi) source CVD, where two or more precursors are used.

Solid materials interact chemically with their environment at the surface; therefore changing the properties of the surface changes the chemistry of the material. Thin films allow the surface properties of a material to be drastically altered without changing the bulk properties, so application of a thin film with useful properties, such as catalysis or variable colour, effectively imparts these properties to the substrate. One of the benefits of CVD is that it can deposit films onto a variety of substrates, so through the use of thin films one can envisage self-cleaning steel or colour changing plastic.

Glass was the substrate of choice for the studies reported here because of its thermal stability, ease of analysis and primarily because of potential commercial applications. Online CVD coating of glass as it is made is now a mature industrial application. Many commercial coatings are now

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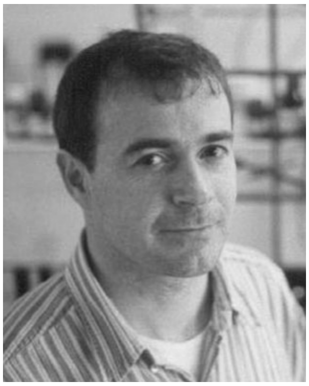

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made in this way including Pilkington Activ™ (TiO_2) and Pilkington K glass (doped SnO_2). The big advantages of the CVD approach to these materials is that they do not require expensive off-line processing and that the coatings are hard wearing, exceptionally adhesive and offer key functional properties, such as self-cleaning and solar control.

1.2 Atmospheric pressure CVD (APCVD)

APCVD refers to a specific technique that is sometimes known as thermally activated APCVD. The precursors used in APCVD are gas phase at room temperature, or are heated to convert them into the gas phase and then transported to the substrate by a flow of nitrogen. The substrate is heated to cause reaction of the precursors, with the deposition carried out under atmospheric pressure. Precursors for APCVD therefore need to be volatile and reasonably thermally stable; small, monomeric, neutral inorganic compounds are the most common choice. Using volatile precursors, high molar concentrations can be achieved in the reactor, leading to rapid film growth rates. Growth rates of up to 3 μm min^{-1} are achievable, meaning that most depositions need last only 1 min or less. The flow rates and temperatures of each precursor can be altered independently, allowing control of reactant concentrations, which may have an effect on growth rate and film stoichiometry.

1.3 Low pressure CVD (LPCVD)

Similarly to APCVD, this technique should perhaps be known as thermally activated LPCVD. The precursors are typically solid, but may also be liquid, and are heated to convert them to the gas phase under reduced pressure (typically 10^{-2} Torr). The substrate is heated to a higher temperature, causing reaction of the precursors. The reduced pressure means that precursors need not be heated as strongly as in APCVD, so less thermally stable precursors can be used. Although dual source LPCVD is possible, it is more suited to single source precursors.

In LPCVD the precursor vapour diffuses to the substrate rather than necessarily being transported *via* a carrier gas; growth rates are typically very slow in LPCVD: 5–20 nm min^{-1} is typical. Therefore depositions usually take several hours to perform.

1.4 Aerosol assisted CVD (AACVD)

AACVD differs from LPCVD and APCVD in that the precursor is not vaporised, at least not in the transport step. A solution of the precursor is atomised by an ultrasonic transducer, producing an aerosol mist, which is then transported to the reactor by a flow of carrier gas such as nitrogen. Precursors therefore need not be volatile but instead soluble in a suitable solvent (acetone, toluene, water and acetonitrile have been used successfully, as well as many others). The substrate is heated, and the deposition is performed at atmospheric pressure. Growth rates are intermediate between those found for APCVD and LPCVD, and are typically 15–30 nm min^{-1}, with depositions typically taking around 20 min.

1.5 Hot-wall and cold-wall reactors

The heating of the substrate in the reactor may be achieved in two main ways. In a cold-wall reactor, only the substrate is directly heated, meaning that the uninsulated walls of the reactor are at a lower temperature. The advantage of this method is that reaction is more likely to occur on the hot substrate than the cold walls. In addition, the temperature gradient within the reactor causes solid particles to be repelled from the hot substrate as a result of asymmetrical Brownian motion. This is known as the thermophoretic effect, and to some extent helps prevent CVD 'snow', produced by premature gas phase reaction, from being incorporated into the growing film. The cold-wall reactors used in most of the studies reported here consist of a horizontal carbon heating-block, upon which the substrate is placed, encased within a quartz cylinder. The reactor is capped by stainless steel end plates, which can be removed to allow loading of the substrate. This type of reactor was used for both APCVD and AACVD experiments.

The LPCVD experiments described here were primarily carried out in a hot-wall reactor. In this set-up, the reactor is placed inside a furnace that maintains a constant temperature throughout the reactor. If they are present at all, thermal gradients are much smaller than in the cold-wall reactor, and hence the beneficial thermophoretic effect is not present. However, hot-wall reactors can be very simple in design: a length of glass tubing sealed at one end, a tube furnace and a vacuum pump.

1.6 Single source and dual source CVD

Single source precursors must necessarily contain all the elements present in the target film. A precursor for the deposition of a transition metal compound MX is commonly a complex containing M–X bonds, for example metal phosphine complexes are used to deposit metal phosphides. It is possible to engineer the precursor to achieve a fast, clean reaction, for example by using good leaving groups or chelating ligands to strengthen M–X bonds. The mechanism of decomposition can often be deduced from thermogravimetric analysis or consideration of the leaving group chemistry. Examples of these strategies and their outcomes are described in this review.

Dual source precursors are generally chemically simpler than their single source counterparts. The deposition of MX can be achieved by the use of a precursor containing M, often a reactive chloride complex, and a precursor containing X, usually an organic compound. The mechanism is usually very difficult to deduce, as it is rarely clear when the M–X bond forms, and whether either or both of the precursors have already decomposed beforehand. Thus it is less practical to engineer precursors, an empirical approach is more suitable. An exception is when dual source precursors can be found to imitate single source precursors. For example, bis(phosphine) adducts of titanium(IV) chloride were used as single source precursors for TiP. A dual source approach, using titanium(IV) chloride and a phosphine as separate precursors also yielded TiP films. Presumably, the adduct forms *in situ* in the reactor,

Table 1 Deposition parameters and film properties of titanium nitride and titanium phosphide thin films

Target material	Precursor 1	Precursor 2	CVD method	Substrate temperature range (°C)	Appearance	Maximum growth rate (nm min^{-1})	TiE_x composition range (E = N, P)	Film resistivity (mΩ cm)	Reference
TiN	$TiCl_4$	$HN(SiMe_3)_2$	AP	350–550	Silver, metallic	300	0.85–1.00	[a]	2
TiN	$[TiCl_2(N^tBu)(py)_3]$	—	LP	600	Gold, metallic	15	1.00	0.2	3
TiN	$TiCl_4$	N_2	PE	530	—	50	[a]	[a]	7
TiN	$Ti(NMe_2)_4$	NH_3	LP	200–450	—	[a]	1.2	0.25	6
TiN	$Ti(NEtMe)_4$	N_2	PE	550	Dark grey	[a]	[a]	[a]	5
TiN	$Ti(NEtMe)_4$	NH_3	AP	350	—	60	0.9	2.0	4
TiP	$TiCl_4$	$P(SiMe_3)_3$	AP	500–550	Gold, metallic	25	1.10	3	13
TiP	$Ti(NMe_2)_4$	H_2PCy	AP	400–550	Gold, metallic	235	0.91–1.00	1.5	14
TiP	$[TiCl_4(PCyH_2)_2]$	—	LP	550	Gold, metallic	5[b]	1.05	[a]	15
TiP	$[TiCl_4(PCy_2H)]$	—	LP	550	Black/gold	5[b]	1.00	[a]	15
TiP	$[TiCl_4(PCy_3)_2]$	—	LP	550	Black	5[b]	0.5–0	Insulating	15
TiP	$[TiCl_4(dppm)]$	—	LP	550	Gold, dull	5[b]	0.5	260	15
TiP	$[TiCl_4(dppe)]$	—	LP	550	Black	5[b]	0[c]	300	15
TiP	$TiCl_4(PCyH_2)_2$	—	LP	350–600	Silver, metallic	[a]	1.1	0.4	10
TiP	$TiCl_4$	PCl_3	AP	1050	—	[a]	[a]	[a]	9

[a] Not measured. [b] Approximate values, growth rate not measured for every film. [c] No P detected in film.

and then goes on to deposit TiP in the same way as the single source precursor.

2. CVD of titanium nitride, phosphide, oxide and sulfide thin films

2.1 Titanium nitride thin films

Titanium nitride (TiN) is a hard, metallic material, which is used in a number of applications. Examples include protective coatings, conducting layers and heat mirrors. TiN displays stoichiometries ranging from $TiN_{0.42}$ to $TiN_{1.2}$, as the N atoms occupy interstitial sites in the close packed Ti lattice.[2] The bulk resistivity of 22 μΩ cm in $TiN_{1.0}$ is lower than in titanium metal.[2] Titanium nitride films have been prepared using both dual source APCVD and single source LPCVD. Table 1 summarises the deposition parameters and film properties discussed in this section.

The APCVD reaction of $TiCl_4$ and $HN(SiMe_3)_2$ produced silver coloured, adherent coatings at substrate temperatures of 350–550 °C.[2] Films deposited at 400 °C and above were crystalline by XRD. All films were highly reflective to red and near IR light, as expected of TiN. The reflection spectrum of a film deposited at 550 °C has a maximum at 990 nm, where 55% of incident light is reflected. The position of the reflection maximum was dependent on the temperature of deposition, and is related to the degree of crystallinity of the films. The composition varied with deposition temperature. Stoichiometric $TiN_{1.00}$ was only deposited at 350 °C; at higher substrate temperatures, the composition fluctuated between $TiN_{0.85}$ and $TiN_{0.95}$, with no obvious trend. Some oxygen was present in the bulk of the film, although neither silicon, carbon nor chlorine could be detected, demonstrating the clean decomposition of the precursors to TiN. The mechanism probably proceeds by the elimination of Me_3SiCl, although this species has not been directly detected.

The LPCVD reaction of titanium imido complexes of the form $[TiCl_2(NR)(L)_x]$ gave TiN films at a substrate temperature of 600 °C.[3] A wide range of R groups and mono- and tridentate L ligands were used.[3] In summary, the quality of the films depended on the nature of the R groups and the lability of the L ligands. It appeared advantageous to form a strong Ti–NR bond with electron donating rather than withdrawing R groups. The R group should be a good leaving group, as should the L ligands, therefore monodentate ligands are superior to chelating ligands. Stoichiometric, crystalline $TiN_{1.00}$ films were produced from $[TiCl_2(N^tBu)(py)_3]$, whereas inferior films were produced from $[TiCl_2(N^tBu)(Me_3[9]aneN_3)]$ ($Me_3[9]aneN_3$ stands for tris(*N*-methyl)triamine-1,4,7 triazacyclononane), which contains a tridentate ligand rather than three monodentate ligands, and worse films still from $[TiCl_2(NC_6F_5)(Me_3[9]aneN_3)]$, with an electron withdrawing R group. It should be noted that since the decomposition of the precursor proceeds through elimination of the L ligands, weaker Ti–amine bonds and stronger Ti–imido promote TiN film formation. It should therefore be expected that the imido nitrogen forms the TiN film whilst the amine leaves as a waste product. This work indicated that choice of precursor was of key importance in determining the pathway of the single source deposition and that the relatively easy to prepare $[TiCl_2(N^tBu)(py)_3]$ was the best precursor evaluated.

Alternative routes to TiN have been investigated by several research groups, examples of which are given in Table 1. Tetrakis(dialkylamino)titanium $[Ti(NR_2)_4]$ ($R_2 = Me_2$, MeEt, Et_2) is a popular family of precursors which can be used either in APCVD or plasma enhanced (PE) CVD, and as single or dual source precursors.[4–6] In APCVD studies, ammonia is used as the second precursor, although $[Ti(NMe_2)_4]$ (TDMAT) can deposit TiN films as a single source precursor, although reaction with NH_3 reduces carbon and oxygen contamination and increases the density of the films.[4] Mass spectroscopic studies of the decomposition of TDMAT and $[Ti(NEt_2)_4]$ (TDEAT) at elevated temperatures suggested a radical chain reaction initiated either by homolytic Ti–N bond cleavage or hydrogen radical attack, showing a possible route to single source deposition.[5] Presumably the higher levels of carbon contamination in the TiN films produced from the single source route is due to incomplete decomposition of the amino ligands. Correspondingly, the use of ammonia reduced carbon content, since the reactions of titanium precursors and ammonia are expected to be rapid at the reactor temperatures.[6]

Plasma enhanced CVD using $TiCl_4$ and N_2 has also been used to deposit TiN coatings.[7] An electrical discharge causes activation of N_2, which reacts forming TiN and probably Cl_2.

2.2 Titanium phosphide thin films

Titanium phosphide (TiP), like TiN, is a hard, metallic material, which is used as a protective coating or conducting layer. It has a lower melting point and higher bulk resistivity (3400 μΩ cm) than TiN.[8] Early work on the CVD of TiP utilised $TiCl_4$ and PCl_4 precursors, at substrate temperatures in excess of 1000 °C.[9] Later work by Winter *et al.* produced the first single source TiP precursor, $TiCl_4(PCyH_2)_2$, which produced TiP films by LPCVD at 350–600 °C.[10] Our laboratory has built upon this work with a systematic study of single source LPCVD precursors, which is described below.

Titanium phosphide films have been prepared by several dual source APCVD routes. All TiP films mentioned below suffered from oxidation of the surface when exposed to air. This resulted in a thin TiO_2 layer, which in all cases could be removed by argon sputtering during XPS analysis, or identified using Rutherford backscattering (RBS), revealing only Ti and P beneath. In most cases, this layer was no more than 50 nm thick. The presence of oxygen only at the surface shows that the oxidation occurs after, rather than during, the deposition process, furthermore the oxidation that these films undergo is self-limiting to just the uppermost parts of the film. The parameters for each CVD process described in this section and the properties of the films produced are summarised in Table 1.

The APCVD reaction of $TiCl_4$ and RPH_2 (R = ^{t}Bu, Ph, Cy) gave reflective, silver coloured, adherent coatings at substrate temperatures of 400–500 °C.[11] All films were conducting with a metallic lustre, and crystalline films could be formed from all three phosphine precursors at 550 °C. The composition of the films, as determined by EDAX and electron probe analysis, ranged from $TiP_{1.00}$ to $TiP_{1.30}$. Stoichiometric $TiP_{1.00}$ was deposited using ^{t}BuPH$_2$ at 550 °C, while the other phosphines deposited phosphorus rich films. The minimum substrate temperature needed to deposit films was 400, 450 and 550 °C for R = Cy, ^{t}Bu and Ph, respectively. Film growth rates also varied significantly with the R group in the order ^{t}Bu $\approx$ Cy $>$ Ph, all other conditions being equal. The Cy and ^{t}Bu groups can decompose to cyclohexene and isobutylene respectively, whereas this pathway is not available to Ph. Thus it is thought that, in this case, Cy and ^{t}Bu are more labile. A mechanism based on the formation of an adduct, $[TiCl_4(PRH_2)_2]$, and its subsequent decomposition through loss of HCl and RCl or RH has been proposed, which mirrors the chemistry seen in the solution phase (Fig. 1). Indeed, such adducts have been used as single source LPCVD precursors and it is not unreasonable to suggest that the same mechanism operates in both cases.[12]

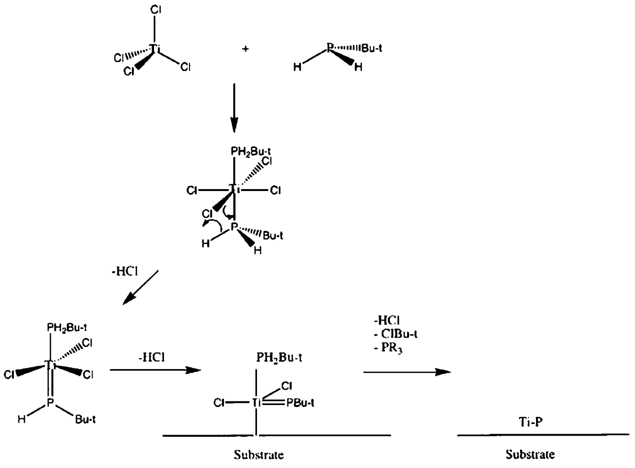

Fig. 1 Gas phase adduct formation and subsequent decomposition of $TiCl_4$ and phosphines during the deposition of TiP thin films by dual source APCVD.

The APCVD reaction of $TiCl_4$ and $P(SiMe_3)_3$ gave reflective, gold coloured, adherent coatings at 500–550 °C.[13] The films were crystalline and slightly phosphorus rich (composition $TiP_{1.1}$ determined by EDAX). The growth rate was 25 nm min^{-1}, which is exceptionally slow for an APCVD process. It is possible that the very bulky nature of the phosphine hinders titanium–phosphine adduct formation. Interestingly, in solution the reaction of $TiCl_4$ and $P(SiMe_3)_3$ yields a Ti(III) adduct of formula $[TiCl_3(P(SiMe_3)_3)_2]$ rather than the Ti(IV) adducts produced from RPH_2.[13] In contrast to the Ti(IV) adducts, the Ti(III) adducts proved to be poor LPCVD precursors, however, as noted above, the phosphine groups investigated were tertiary phosphines for Ti(III) and primary phosphines for Ti(IV). The nature of the phosphine with an accessible P–H bond probably has more bearing on the reaction than the oxidation state of the titanium precursor.

The APCVD reaction of $Ti(NMe_2)_4$ and $CyPH_2$ gave reflective, gold coloured adherent films at substrate temperatures of 400–550 °C.[14] All films were amorphous to X-rays, even those deposited at 550 °C. However, TiP peaks were observed in the Raman spectrum of films deposited at 450 °C. The growth rate of films deposited at 450 °C was highly dependent on the molar ratios of the precursors, which was varied from Ti : P 1 : 30 to 50 : 1, as shown in Fig. 2. The growth rate is greatest at a Ti : P precursor ratio of 1 : 5, and decreases as the ratio is changed in either direction, ranging from 70–195 nm min^{-1}. The composition of the films, on the other hand, was unaffected by changes in the precursor ratios, remaining close to $TiP_{1.00}$ in all cases. Some sub-stoichiometric compositions were recorded, *i.e.* TiP_{1-x}, $x > 0$, although this is probably an anomalous measurement due to the small layer of titanium dioxide, rather than a true TiP_{1-x} phase. The mechanism of the reaction was not determined, although the gas-phase formation of an adduct of the type $[Ti(NMe_2)_4(PCyH_2)_2]$ seems a likely first step, given the similar reaction mechanisms outlined above. The amido ligands may then depart as $HNMe_2$ and the Cy groups as cyclohexene. The invariance of film composition despite large changes in the

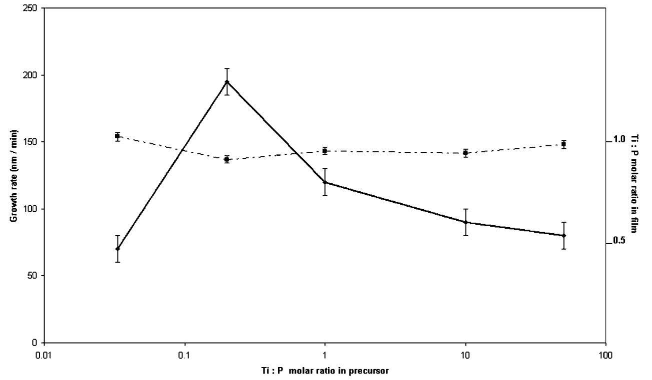

Fig. 2 Variation in growth rate (solid line) and composition (dashed line) of TiP films deposited from different precursor ratios of Ti : P. Growth rate is highly dependent on the precursor ratio, while the composition is largely independent.

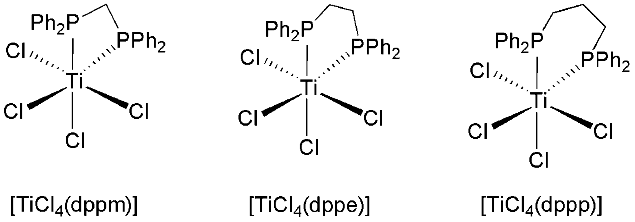

Fig. 3 Single source precursors used to grow TiP thin films.

precursor ratio points to a single and relatively clean decomposition pathway. It is interesting to note that TiP rather than TiN is the major product of deposition, despite the presence of Ti–N bonds in the precursor.

Carbon contamination was present in all the TiP films formed from $Ti(NMe_2)_4$—it was highest (14.3 atomic%) in the film deposited from a Ti : P precursor ratio of 1 : 30, probably due to the higher concentration of carbon in the precursor mix (from the Cy groups). All other films, which were deposited from a lower proportion of phosphine, had a roughly constant level of carbon contamination of approximately 6.5 atomic%. Nitrogen was observed by WDAX (wavelength dispersive analysis by X-rays) at around 3 atomic% in all films, although the nitrogen peak is partially coincident with the Ti peak, so there is some error in this reading. XPS detected an oxidised surface layer as expected, and multiple Ti environments, which were tentatively assigned to TiP, $TiPO_4$, TiO_2, TiN and TiC.

Single source LPCVD routes to TiP using precursors of the form $[TiCl_4L_n]$, where L is a series of monodentate and bidentate phosphine ligands, have been investigated.[15] Where $n = 2$, L = H_2PPh, $HPPh_2$, PPh_3, H_2PCy, $HPCy_2$, PCy_3. Where $n = 1$, L = $Ph_2P(CH_2)PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) as shown in Fig. 3. Table 1 summarises the results of the depositions. Only precursors containing PCy_3, $HPCy_2$, H_2PCy, dppm or dppe deposited any film at all, and only precursors containing H_2PCy or $HPCy_2$ deposited TiP films of comparable quality to the APCVD films discussed above. As is typical of LPCVD, the growth rates were much slower than those found in APCVD. Growth rates of 5 nm min^{-1} were observed, with depositions taking around 4 hours to complete. When analysed, all films had an oxidised surface layer, with a TiP layer exposed by ion etching or RBS. The range of precursors used and their respective success or failure offers some insight into the mechanism. The precursors immediately resemble the titanium chloride–phosphine adducts thought to form in the gas phase during the APCVD reactions described above. There, the decomposition pathway of the phosphine R groups was a key factor in the deposition, for example growth rates varied with R: ^{t}Bu > Cy > Ph. This seems to hold true in the case of the monodentate phosphines: H_2PCy and $HPCy_2$ gave high quality films, while H_2PPh and $HPPh_2$ gave no film at all. In the case of the chelating ligands, the growth rate varied as follows: dppm > dppe > dppp. The films were rather low quality, and the dppp complex gave virtually no film at all. The $[TiCl_4(dppm)]$ complex contains a highly strained four-membered ring; the strain decreases moving to $[TiCl_4(dppe)]$ (five-membered ring) and $[TiCl_4(dppp)]$ (six-membered ring). Ring opening seems an obvious decomposition pathway, and would be more favourable in the smaller, more strained rings. In the dppp complex the chelating ligand is presumably stable enough to avoid decomposition to TiP, even at 550 °C. The monodentate and bidentate ligands should be compared with caution. Although the bidentate complexes gave generally poor films, the monodentate complexes that most closely resemble them, those with phenyl phosphine ligands, gave no films at all. It can be concluded that the bidentate ligands were superior to the monodentate, when comparing like with like.

2.3 Titanium sulfide thin films

Titanium sulfide (TiS_2) is a semiconducting material that has been widely investigated as a cathode material for Li ion batteries. It may also be used as a high temperature solid-state lubricant, due to its layered structure. TiS films have been deposited by dual source APCVD methods and single source AACVD.[16]

The APCVD reaction of $TiCl_4$ with $HS(CH_2)_2SH$, $S(SiMe_3)_2$, $(S^tBu)_2$ and ^{t}BuSH each resulted in adherent, gold coloured, reflective films at substrate temperatures of 275–600 °C.[16] Each precursor was able to produce crystalline films at 350 °C or above, except $S(SiMe_3)_2$ which produced crystalline films at 450 °C and above. Some TiS_3 was detected at lower deposition temperatures when $(S^tBu)_2$ was used. Perhaps the most interesting aspect of these depositions is the similarity of the films produced by the different sulfur containing precursors. The morphology (determined by SEM), thickness and substrate coverage were very similar for all precursors used. Apart from some change in the temperature required for crystallinity, and the presence of sulfur rich phases, the performance of the sulfur precursors was virtually identical. This is perhaps surprising, given the significant differences in growth rate, film composition and colour seen in depositions of TiP from $TiCl_4$ and PRH_2 when different phosphines were used, as discussed above.[11] The mechanism may proceed through coordination of the sulfur precursor to titanium, presumably after the breaking of the sulfide bond in the case of $(S^tBu)_2$, as has been observed in the other APCVD reactions discussed above. In fact all of the sulfur reagents used are known to form thiolate complexes of titanium with the exception of $S(SiMe_3)_2$. The invariance of deposition with changing precursor suggests that the reaction with $TiCl_4$ is very fast, rendering differences in the precursors inconsequential to the final result. On the other hand, the similar behaviour of all four precursors may indicate a decomposition of the sulfur precursor before reaction with $TiCl_4$.

In contrast, the result of the AACVD reaction of $Ti(NMe_2)_4$ with ^tBuSH, $S(SiMe_3)_2$ and $(S^tBu)_2$ was highly dependent on which sulfur precursor was used.[17] Depositions using ^tBuSH gave films from 175–500 °C, with compositions ranging from $TiS_{2.1}$ to $TiS_{1.3}$. Depositions using $(^tBuS)_2$ gave $TiS_{1.6}$ films at 600 °C, but at lower temperatures the sulfur composition fell further still. This is thought to be due to oxygen inclusion in the film, although TiO_2 was not detected by Raman or XRD, indicating that, if present, the oxide phase is amorphous. The use of $S(SiMe_3)_2$ produced films containing little sulfur. These films were mostly composed of titanium carbonitride ($TiC_{0.5}N_{0.5}$), which is the product formed from the APCVD of $Ti(NMe_2)_4$ alone,[14] suggesting that no reaction had taken place between the precursors.

A handful of other CVD routes to TiS_2 have been reported in the literature. For example, the LPCVD reaction of $Ti(S^tBu)_4$ resulted in stoichiometric $TiS_{2.0}$ films with little oxygen contamination at substrate temperatures of 110–350 °C.[18] Mass spectroscopic analysis of the exhaust gasses revealed isobutylene, *tert*-butyl thiol and H_2S as major by-products. The presence of isobutylene suggests a β-hydrogen elimination reaction, the hydrogen may be transferred to a neighbouring thiolate ligand producing the *tert*-butyl thiol, which is also observed in the exhaust.

2.4 Titanium dioxide thin films

Titanium dioxide (TiO_2) is an important commercial material due to its absorption of UV light (used in sunscreens), brilliant white colour (used in paints), non-toxicity (used as a food additive) and photovoltaic properties (used in solar cells).[19] However, it is the self-cleaning properties of TiO_2, specifically in its use in glazing applications that have attracted renewed interest; self cleaning windows have recently been launched as commercial products by a number of companies worldwide. The self-cleaning properties of TiO_2 are twofold, and both are activated by near-UV light. Firstly, photocatalysis chemically removes dirt by oxidising adsorbed organic material. Secondly, the superhydrophilic surface causes dirt to be physically removed, as rainwater sheets off the surface carrying dirt with it. Theoretical explanations of these phenomena are based on the excitation of valence band electrons by near UV light; detailed descriptions can be found elsewhere,[19,20] but from a CVD perspective it should be noted that film thickness, crystallinity and morphology are all important factors.

Although the CVD of TiO_2 is very well established,[21] as is the study of the surface properties and photocatalysis of monolithic TiO_2, it is curious to note that literature concerning the self cleaning properties of CVD titania thin films is much more limited.[22] This is more surprising given the recent successful commercialisation of such coatings worldwide, as mentioned above. Our group has studied the self-cleaning properties of a variety of TiO_2 coatings, including CVD coatings.[19,22]

The APCVD reaction of $TiCl_4$ and MeOH, EtOH, ^iPrOH and H_2O gave adherent, colourless films at substrate temperatures of 500–600 °C.[19] The different precursors all gave very similar results; all were crystalline, with only a single phase of anatase (TiO_2) present, and all gave similar growth rates of 300 nm min^{-1}. The bulk composition of the films was $TiO_{2.0}$. Since $TiCl_4$ reacts at room temperature with all of the precursors mentioned, the reaction under APCVD conditions at 500 °C is expected to be rapid, which may explain the similar results obtained with each oxygen containing precursor. Despite the fast reaction rates, the films are adherent and non-hazy, not powdery as can result from extensive gas phase reaction and CVD 'snow'.

2.5 The role of the precursor in deposition of Ti containing films

The success or failure of the depositions described in Sections 2.1–2.4 depends upon the precursors. Considering the APCVD precursors, and putting aside volatility, which is a prerequisite for APCVD, the next most critical factor is the decomposition pathway. Two titanium precursors were examined. $TiCl_4$ proved an excellent precursor for all four titanium thin films: TiN, TiP, TiO_2 and TiS_2. It is able to form adducts of the type $[TiCl_4(L)_x]$, as with phosphines,[11] as a first step in the CVD reaction. The very facile removal of chlorine as HCl or alternatively RCl is also an advantage—no chloride contamination was found in any film deposited from $TiCl_4$. Reactions of $TiCl_4$ are characterised by high growth rates and high film crystallinity, sometimes regardless of the other precursor used. In depositions of TiS_2 and TiO_2 using $TiCl_4$, the nature of the sulfur or oxygen precursor could be varied, in the case of sulfur quite widely (thiol, dithiol, disulfide) without appreciably changing the resulting film or growth rate. In these cases the reaction is fast compared to the transport of reactants to the substrate, and is known as the mass transport limited regime. $Ti(NMe_2)_4$ was generally less effective than $TiCl_4$, depositing TiP and TiS_2 at slower growth rates with the same co-reactant. Additionally, depositions using $Ti(NMe_2)_4$ were highly dependent on the nature of the second precursor. In depositions of TiS_2, a wide variety of precursors gave almost identical films when reacted with $TiCl_4$ but produced a wide range of compositions with $[Ti(NMe_2)_4]$, and one, $S(SiMe_3)_2$, did not react at all. The outcome of the deposition therefore is being determined by the rate of reaction of the precursors. This is the reaction rate limited regime, where the reaction between precursors is slow compared to the transport of precursors to the substrate. The reasons for the slower reaction rate are that the larger steric bulk of the (NMe_2) ligands hinders adduct formation, and the fact that $HNMe_2$ elimination is less facile than elimination of HCl.

Of the non-metal precursors used, *i.e.* precursors for the N, P, O and S atoms in the films, the less bulky molecules tended to perform better. With $TiCl_4$, PH_2Cy gave better films at a

Table 2 Deposition conditions and film properties of tungsten oxide thin films

Precursor 1	Precursor 2	CVD method	Substrate temperature range (°C)	Appearance	Maximum growth rate (nm min^{-1})	WO_x composition range	Reference
WCl_6	$(CH_3CO)_2O$	AP	450–625	Blue or yellow	1000	2.8–3.2	23
WCl_6	EtOH	AP	625	Blue	800	3.05	23
WCl_6	MeOH	AP	625	Blue	300	[a]	23
WCl_6	H_2O	AP	625	Yellow	225	[a]	23
WCl_6	CH_3CO_2H	AP	625	Yellow	200	[a]	23
$WOCl_4$	CH_3CO_2Et	AP	350–650	Blue or yellow	200	2.9–3.0	27
$WOCl_4$	EtOH	AP	350–650	Blue or yellow	200	2.9–3.0	14
$[^nBu_4N]_2[W_6O_{19}]$	—	AA	410	Blue	17	3[b]	30
$W(OC_6H_5)_6$	—	AA	450–600	Blue	22	2.9–3.0	28
$W(OC_6H_4F)_6$	—	AA	300–450	Blue	17	2.9–3.0	28
$W(OC_6H_3F_2)_6$	—	AA	300–450	Blue	17	2.9–3.0	28
WF_6	H_2O	AP	200–700		>16	3.0	25
$W(CO)_6$	O_2	AP	200–300	Blue	345	2.7–3.0	26

[a] Could not be determined, as significant quantities of water were present in the films. [b] Approximate value.

faster growth rate than $P(SiMe_3)_3$, a much bulkier phosphine. Bulk clearly plays a role in the initial coordination of the non-metal precursor to the metal complex, but cleavage of the E–R bond (E = N, P, O, S) is also important.

Large variations were seen in the quality of films deposited from single source precursors with similar volatilities and similar coordination environments around the metal. In several cases, the single source precursors closely resembled the adducts thought to form during the dual source deposition of the same material, *e.g.* the single source precursor $[TiCl_4(PCyH_2)_2]$ and the dual source precursors $TiCl_4 + PCyH_2$. Again, decomposition pathways are important; the $[TiCl_4(PCyH_2)_2]$ complex, which contains an H atom in the phosphine, easily liberates HCl on decomposition and gave a good quality TiP film, whereas $[TiCl_4(PCy_3)_2]$ failed to give a film. Precursors containing chelating phenyl phosphine ligands gave poor quality films, although those with monodentate phenyl phosphine ligands gave no film at all. This can be explained by the chelate effect, which is expected to strengthen the Ti–P bond, and may prevent loss of the phosphine from the complex. The ring strain also encourages $P–CH_2$ bond cleavage, allowing the complex to decompose to TiP.

3. CVD of tungsten oxide thin films

Tungsten trioxide is pale yellow when fully oxidised, but dark blue in the sub-stoichiometric form WO_{3-x}, $x \approx 0.1$. Interconversion of the two forms, causing a change in colour, can take place on application of an electric current, or irradiation by light of a suitable wavelength.[23,24] The electrochromic and photochromic properties of tungsten oxide suggest several possible applications, especially in thin film form, such as smart windows, anti-dazzle mirrors and information displays.[23,24] CVD of WO_3 has traditionally been carried out using reactive tungsten halides, usually WF_6, or tungsten carbonyl in an oxygen rich atmosphere.[25,26] Our group has examined the use of WCl_6 and novel tungsten precursors to deposit WO_3 films. Table 2 shows the deposition conditions and results of these experiments, as well as those carried out by other groups.

The APCVD reaction of WCl_6 and various oxygen containing precursors deposited tungsten oxide films of varying quality at temperatures of 450–625 °C.[23] Very high flow rates were needed to deposit films from WCl_6, which is perhaps the reason it had not previously been identified as a suitable precursor for tungsten oxide films. Furthermore the material has a very narrow usable temperature range when used as precursor, with the melting and decomposition temperatures being separated by 20 °C. The different oxygen precursors investigated (ethanoic anhydride, ethanol, methanol, water and ethanoic acid) produced tungsten oxide with different stoichiometries at varying growth rates. Growth rates at 625 °C ranged from 200–1000 nm min^{-1} with ethanoic anhydride giving the fastest growth and ethanoic acid the slowest. SEM showed that the fastest growth rates were not due to more porous, less dense films, but genuinely due to a greater deposition of material. However, it should be noted that in the case of ethanoic anhydride, the faster growth rate could be due to a greater molar flow of the precursor. Other precursors investigated, ethyl ethanoate, 2-propanol and 2-methyl-2-propanol, failed to deposit a film.

The stoichiometries of the films, and correspondingly their colours, also varied with precursor. The exact stoichiometries could not be determined in some cases, due to the incorporation of a large amount of water in the films (observed by FT-IR), however the colour of the film could be used as a guide. Yellow, fully stoichiometric WO_3 films were deposited at lower temperatures. Some precursors, ethanol and methanol, deposited blue films at 625 °C, while others, ethanoic anhydride, water, and ethanoic acid, continued to deposit yellow films even at 625 °C. Variation in stoichiometry and colour with temperature has been observed in other tungsten oxide depositions (see below), and is usually explained by the more rapid reaction at higher temperatures.[24] Indeed, the growth rates, and hence rates of reaction, of the blue films deposited from ethanol and methanol were greater than those of the yellow films deposited from ethanoic acid and ethyl ethanoate. Ethanoic anhydride is an anomaly in the trend, giving a yellow film at 625 °C despite having the fastest growth rate. This might be explained by the greater molar flow of ethanoic anhydride

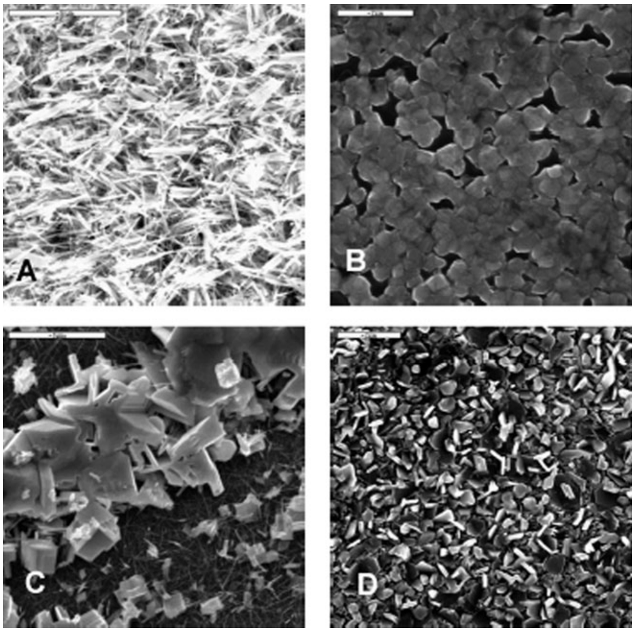

Fig. 4 SEM micrographs of films deposited by APCVD of WCl_6 and A: ethanol; scale bar: 5 microns, B: ethanoic acid; scale bar: 2 microns, C: methanol; scale bar: 5 microns, D: water; scale bar: 2 microns, at 625 °C.

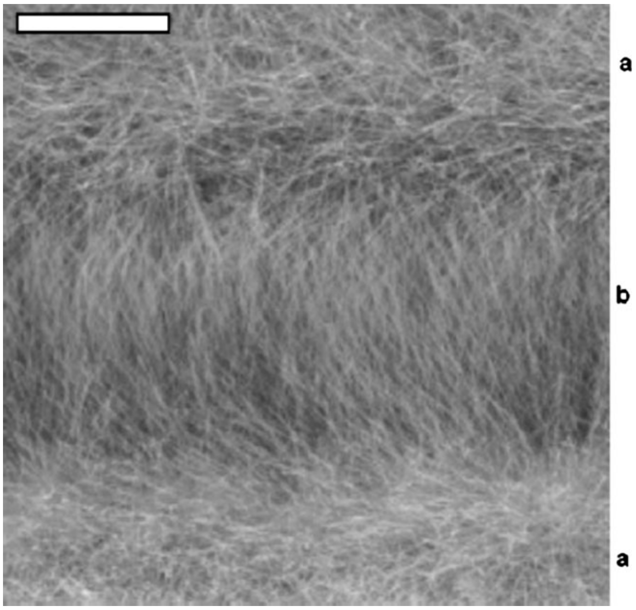

Fig. 5 SEM micrograph of a WO_3 film grown in an electric field of 1 V rms at 50 Hz; scale bar: 20 microns. Two distinct areas of deposition are visible: (a) orientated fibrous growth is obtained in the electrode gap; (b) more randomly orientated fibres are observed on the electrode surface.

used, and the larger proportion of oxygen in the precursor, which results in an oxygen rich atmosphere.

SEM revealed very different morphologies in films deposited from different precursors, as shown in Fig. 4. Ethanol and methanol deposited a dense mat of thin micron scale needles, while water deposited round individual micron scale platelets, and ethanoic acid deposited fused platelets. Despite these differences, all films gave an XRD pattern consistent with monoclinic WO_3. The mechanism of the reaction is unknown, but some carbon contamination in the films points to extensive decomposition of the oxygen precursors. Elimination of HCl is likely, and correspondingly no chlorine contamination was observed in the films. The need for very high flow rates shows that the reaction is very fast, or the reactive species that deposits the film is very short lived.

A second APCVD route to tungsten oxide is through the reaction of $WOCl_4$ with ethyl ethanoate or ethanol.[27] The two oxygen precursors gave very similar results. Films were deposited from 350–650 °C in both cases, with yellow, fully stoichiometric films produced at lower temperatures (350–450 °C) and blue, sub-stoichiometric films produced at higher temperatures. Growth rates of 200 nm min^{-1} were achieved by both precursors. It is interesting to note that $WOCl_4$ was able to deposit tungsten oxide films with ethyl ethanoate while WCl_6 was not. It is hard to rationalise this without more knowledge of the reaction mechanism, although the W–O bonds already present in $WOCl_4$ may make the deposition more facile.

The AACVD reaction of $[W(OAr)_6]$ (Ar = C_6H_5, C_6H_4F, $C_6H_3F_2$) in acetone and toluene resulted in tungsten oxide films at substrate temperatures of 300–500 °C.[28] AACVD depositions at 300 °C resulted in amorphous films in all cases, while at higher temperatures XRD indicated that crystalline films were produced. Yellow films were not deposited, even at the lower temperatures. Both toluene and acetone were used as solvents with $[W(OC_6H_5)_6]$ while only toluene was used with the fluorinated precursors. In the case of $[W(OC_6H_5)_6]$ the use of toluene or acetone made little difference to the growth rate or composition of the film. This suggests that the solvent does not play an important role in the deposition, and further that acetone does not act as an oxygen source in this case. An oxygen source was necessary in the APCVD reactions using WCl_6 or $WOCl_4$. The precursors containing fluorinated aryl groups gave similar growth rates to the unfluorinated precursor (Table 2), showing that the reaction is not sensitive to small changes in the ligand electronic properties.

In a second set of experiments, the effect of an electric field on the morphology of WO_3 films deposited from $[W(OC_6H_5)_6]$ was investigated.[29] The films were deposited on an alumina substrate with a micron scale pattern of interdigitated gold electrodes, heated to 600 °C. The use of alternating and direct currents gave startlingly different results; an alternating current produced a random needle-like growth on both positive and negative electrodes, with aligned needles between the electrodes (Fig. 5). A direct current produced selective deposition only on the negative electrode, suggesting a charged gas phase species, or a static charge on the aerosol droplets themselves. An important point to note is that the substrate used was small (3 mm × 3 mm) and heated resistively using the electrodes, rather than using the heating block, as is usually the case. Therefore the overall reactor temperature will be very low, close to room temperature, so it might be possible for the solvent aerosol droplet to reach the substrate before vaporising. It is possible that the aerosol droplets are directed to the negative electrode, although it seems, given the ordered crystal growth seen using an alternating current, that the film growth is also affected by the field.

The AACVD reaction of a polyoxotungstate, $[^n\mathrm{Bu_4N}]_2[\mathrm{W_6O_{19}}]$, dissolved in acetone yielded adherent blue coatings at substrate temperatures above 410 °C.[30] However, the films were formed on the underside of the top plate, a second glass plate placed parallel to the substrate and around 8 mm above it, while no deposition occurred on the substrate. It seems likely that the thermophoretic effect is at work, driving the reactive species away from the hot surface (the substrate) towards the cold surface (top plate). The polyoxotungstate clusters themselves may be large enough to experience the thermophoretic effect, or they may undergo gas phase reaction creating larger particles. However, such particles usually form a powdery, non-adherent coating on the top plate, but in this case much of the film was adherent and resistant to abrasion. The specific polyoxotungstate used has a structure that resembles a fragment of the extended crystalline structure of monoclinic WO_3, so it is likely that any gas phase particles formed would have a similar structure. These fragments can sinter together to form a continuous, adherent film after deposition on the top plate. The films showed a crystalline WO_3 XRD pattern, and Raman spectroscopy showed bands corresponding to W^{5+} ions, consistent with a reduced WO_{3-x} stoichiometry. Heating in air at 550 °C caused the blue films to become yellow, and analysis indicted that oxidation to $WO_{3.0}$ had occurred. This deposition illustrates the ability of AACVD to deposit films from precursors unsuitable for AP or LPCVD, in this case involatile ionic compounds. This is one of the first examples of a precursor designed specifically for AACVD; the technique is usually used as a substitute for AP or LPCVD when a precursor proves involatile or thermally unstable, as in the case of $W(OAr)_6$ discussed above.

Polyoxotungstates containing dopant phosphorus atoms have also been investigated as CVD precursors.[30] The resulting tungsten oxide films contained an amount of P identical to that of the precursor; this is a convenient way to produce films with a well defined level of dopant.

4. Conclusion

This review has focused on the chemical vapour deposition of tungsten oxide and titanium chalcogenides and pnictides. The work illustrates that choice of precursor is of key importance in the process. This is particularly the case for low pressure CVD reactions, where changes in coordination sphere around the metal have a crucial influence on the decomposition pathway and hence the nature of the coating. At atmospheric pressure and as necessitated by volatility requirements, normally a dual source approach is required in which the two elements required for the film are carried by different precursors. Here the choice of precursor chemicals can have a determinant effect, for example, in forming metal phosphide films from $TiCl_4$ and phosphine, electron-donating phosphine groups, with accessible β-hydrogens were of key importance. Whereas in the analogous APCVD reactions to form TiS_2 the specific precursor used had little effect. The dual source APCVD of tungsten oxide showed that the nature of the oxygen source has crucial importance in determining the morphology of the tungsten oxide films produced. Further, in the AACVD reactions to form tungsten oxide films, the morphology of the films can be altered by an external electric field. Precursor choice for the AACVD of tungsten oxide films has been widened to include unconventional ionic polyoxometallate precursors.

The AP-, LP- and AACVD methods described in this review have enabled production of high purity films with a range of properties. Precursor choice and deposition route have a dramatic effect on the growth morphology and functional properties of the films. For example, only fully stoichiometric tungsten oxide grown from WCl_6 and ethanol with a (002) preferred growth orientation where shown to be active photocatalysts. To date this work has been directed by informed empiricism, no predictive calculations have been achieved. Much scope for a detailed mechanistic evaluation of the reactions and for an allied theory exists.

5. Perspectives and future directions

The field of functional coatings is an important and active area of research; with the successful release of self-cleaning and solar control glass, it has also proved to be a profitable one. CVD, with its characteristic fast growth rates and conformal coverage is the perfect tool for deposition of functional coatings and so will certainly find heavy application in this field. In order to develop functional coatings with ever-higher performance it is necessary to achieve ever-greater control of growth rate, stoichiometry and purity. As discussed in this article, the design of precursors and understanding of their decomposition is key to the deposition of high quality films with controllable properties, and therefore trends in precursor design will in future be driven by the requirements of new coatings. Single source precursors typically give superior control of composition, but at present are often limited to use in LPCVD due to low volatility. Development of sufficiently volatile single source precursors will allow use in APCVD, which on a large scale is cheaper and yields higher growth rates. Understanding of reaction mechanism is another important step. Basic kinetic and thermodynamic ideas can be applied generally to a wide range of CVD systems, but often correlate poorly with experiment. So far only a few systems have proved important enough for a detailed analysis of their reaction pathway, such that they can be modelled with any great accuracy. However, these models are highly specific to the system in question. Most studies take the middle ground, using chiefly analogies with solution phase chemistry or similar CVD systems and educated guesses to broadly explain the decomposition of the precursor. Hence there is significant room for new calculations and modelling in this field, indeed progress requires a more analytical approach than the semi-empirical methodology that is used at present.

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