Titanium Phosphide Coatings from the Atmospheric Pressure Chemical Vapor Deposition of $TiCl_4$ and RPH_2 (R = *t*-Bu, Ph, Cy^{Hex})

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Atmospheric pressure chemical vapor deposition of titanium phosphide coatings was achieved on glass substrates from the reaction of $TiCl_4$ and RPH_2 (R = *t*-Bu, Ph, Cy^{hex}) at 450−550 °C. The coatings show good uniformity, surface coverage, and adherence; they passed the Scotch brand tape test and could not be scratched with a brass scalpel. The leading edge of the titanium phosphide films was a deep blue while the bulk of the film was reflective and silver. Growth rates were on the order of 1 μm min^{-1} at 550 °C. The films were crystalline, single phase with a hexagonal cell of a = 3.49(1) Å and c = 11.70(1) Å. Scanning electron microscopy (SEM) revealed surface morphologies consistent with an island growth mechanism. X-ray photoelectron spectroscopy (XPS) binding energy shifts were at 454.6 eV for Ti_{2p} and at 128.6 eV for P_{2p}. Energy-dispersive X-ray analysis (EDXA) and electron probe studies gave elemental ratios that were in agreement indicating in most cases slightly P-rich films, $TiP_{1.2}$, with negligible chlorine incorporation. Raman spectra exhibited bands at 245, 320, and 410 cm^{-1}. Sheet resistance measurements showed typically 10−120 mΩ cm, indicating good conductivity. Rutherford backscattering showed a bulk composition of $TiP_{1.2}$. Optically, the films showed high reflectivity at 1000 nm and showed 5−25% total transmission from 300 to 800 nm. Contact angle measurements were in the range 40−50° for the as made films these showed little change after 30 min of irradiation at 254 nm. All of the films showed negligible photocatalytic activity in the destruction of an overlayer of stearic acid.

Transition metal phosphides have an array of properties that could find commercial application. They are hard, refractory metallic conductors, which in some cases show great resistance to oxidation.[1] Despite this they have found limited use as diffusion barrier layers in semiconductors[2] and as a matrix in phosphoric acid fuel cells.[3] This is in contrast to the corresponding metal nitrides that have extensive technological applications.[4] The main group phosphides InP and GaP have been exhaustively studied and a number of synthetic techniques developed for the formation of thin films.[5]

Kaner et al. have shown that a range of metal phosphides can be made by the solid-state metathesis reaction of MX_4 (M = Ti, Zr, Hf) and Na_3P.[6] The metathesis procedure allows the formation of both the thermodynamically more stable hexagonal phase as well as cubic phases. We have shown that similar metathesis reactions can be used to form a wide range of actinide, lanthanide, main-group, and transition-metal phosphides.[7] The metathesis reactions have the advantage of being relatively simple to perform forming metal phosphides in seconds. Products are readily purified in metathesis reactions simply by washing with an appropriate solvent. Formation of thin films of metal phosphides has received scant attention, especially by chemical vapor deposition.

Dual source CVD methods to TiP coatings have involved the reaction of $TiCl_4$, PCl_3 and H_2 at 850−1050 °C.[8] Sasaki prepared films of composition TiP through

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Table 1. Deposition Conditions and Analysis of the Films Generated from the APCVD of $TiCl_4$ and RPH_2 (R = *t*-Bu, Ph, Cy^{Hex})[a]

substrate temp, °C; RPH_2	nitrogen flow through $TiCl_4$ bubbler, L/min (mol/min)[a]	nitrogen flow through RPH_2 bubbler, L/min (mol/min) [bubbler temp, °C]	nitrogen flow of make up gas, L/min	EDAX and electron probe analysis	Raman peaks (cm^{-1})
450; *t*-Bu	0.3 (0.00186)	0.3 (0.005) [20]	1.0	$TiP_{1.29}$	235, 320, 410
500; *t*-Bu	0.3 (0.00186)	0.3 (0.005) [20]	1.0	$TiP_{1.14}$	240, 320
550; *t*-Bu	0.3 (0.00186)	0.3 (0.005) [20]	1.0	$TiP_{1.00}$	242, 306
550; *t*-Bu	0.3 (0.00186)	0.6 (0.010) [20]	0.7	$TiP_{1.19}$	235, 320
550; *t*-Bu	0.3 (0.00186)	0.9 (0.015) [20]	0.4	$TiP_{1.29}$	235, 320
550; *t*-Bu	0.6 (0.00373)	0.3 (0.005) [20]	0.7	$TiP_{1.26}$	235, 320
550; *t*-Bu	0.9 (0.00560)	0.3 (0.005) [20]	0.4	$TiP_{1.24}$	235, 320
550; Ph	0.6 (0.00373)	1.6 (0.027) [100]	0.2	$TiP_{1.30}$	235, 320
400; Cy	0.4 (0.00248)	0.6 (0.010) [130]	1.0	$TiP_{1.30}$	235, 320
450; Cy	0.4 (0.00248)	0.6 (0.010) [130]	1.0	$TiP_{1.28}$	235, 320
500; Cy	0.4 (0.00248)	0.6 (0.010) [130]	1.0	$TiP_{1.14}$	235, 320
550; Cy	0.4 (0.00248)	0.6 (0.010) [130]	1.0	$TiP_{1.14}$	235, 320

[a] $TiCl_4$ bubbler maintained at 80 °C for all experiments.

to Ti_4P_3 by reacting titanium plates with phosphorus at 650−900 °C.[9] Single-source strategies to TiP have been pioneered by Winter et al.[10] They have shown that reaction of $TiCl_4$ with 2 equiv of cyclohexylphosphine in hexane produces an adduct $[TiCl_4(PH_2C_6H_{11})_2]$ that is an ideal precusor for CVD. At 0.1 mmHg and 350−600 °C the precursor formed silver films on silicon and glass substrates. The films were slightly P-rich $TiP_{1.1}$ and were found to be free of carbon and chlorine contamination. The films had metallic properties. SEM analysis showed that the films grown at 600 °C consisted of interlocking hexagonal crystallites. The films were X-ray amorphous. Winter has further developed the single-source approach to the synthesis of niobium phosphide.[11]

Here we report the dual source APCVD of $TiCl_4$ and RPH_2 (R = *t*-Bu, Ph, Cy^{hex}) to form silver films of crystalline TiP.

Experimental Section

Nitrogen (99.99%) was obtained by BOC and used as supplied. Coatings were obtained on SiCO coated float-glass. APCVD experiments were conducted on 90 mm × 45 mm × 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 (60−80 °C) and 2-propanol and then 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 5 °C at 500 °C were noted across the glass substrates. The rig was designed so that four independent gas lines could be utilized. All gas handling lines, regulators and flow valves were made of stainless steel and were $^1/_4$ in. internal diameter except for the inlet to the mixing chamber and the exhaust line from the apparatus that were $^1/_2$ in. 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. Titanium(IV) chloride (99.9%, Aldrich Chemical Co.) was used as supplied and placed into a stainless steel bubbler. The bubbler was heated to 68 °C by a heating jacket and $TiCl_4$ introduced into the gas streams by passing hot nitrogen gas through the liquid. *t*-$BuPH_2$ was supplied by Epichem in a stainless steel container containing valves that could be directly integrated into the CVD system. The *t*-$BuPH_2$ was used as supplied. $Cy^{hex}PH_2$ and $PhPH_2$ were purchased from Strem Chemicals and used as supplied. Exact flows and temperatures for the CVD experiments are listed in Table 1. Streams of $TiCl_4$ (diluted with nitrogen) and RPH_2 (R = *t*-Bu, $Cy^{hex}PH_2$, Ph) were mixed by using concentric pipes of $^1/_4$ in. and $^1/_2$ in. 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 30 min 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. Deposition experiments were timed by stopwatch for typically 60 s. At the end of the deposition the bubbler-line was closed and only nitrogen passed over the substrate. The glass substrate was allowed to cool with the graphite block to ca. 60 °C before it was removed. Coated substrates were handled and stored in air. The large coated glass sample was broken up into ca. 1 cm x 1 cm squares for subsequent analysis by XPS, EDXA, SEM, electron probe, transmission/reflectance, and UV absorption studies. Large pieces of glass (ca. 4 cm × 4 cm) were used for sheet resistance, X-ray powder diffraction, infrared, contact angle, photocatalysis, and Scotch brand tape tests.

X-ray powder diffraction patterns were measured on a Philips X-pert diffractometer using unfiltered (Cu $K\alpha_1$, λ_1 = 1.5045 Å; $K\alpha_2$, λ_2 = 1.5443 Å) radiation and on a Siemens D5000 diffractometer using monochromated $CuK\alpha_1$ radiation (λ_1 = 1.5406 Å). Both diffractometers used glancing incident radiation (1.5°). Samples were indexed using Unit Cell and compared to database standards.[12] SEM/EDAX was obtained on a Hitachi S570 instrument using the KEVEX system. Electron microprobe analysis was obtained on a JEOL EMA and referenced against phosphorus and titanium standards. X-ray photoelectron spectra were recorded with a VG ESCALAB 220i XL instrument using focused (300 μm spot) monochromatic Al Kα 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−

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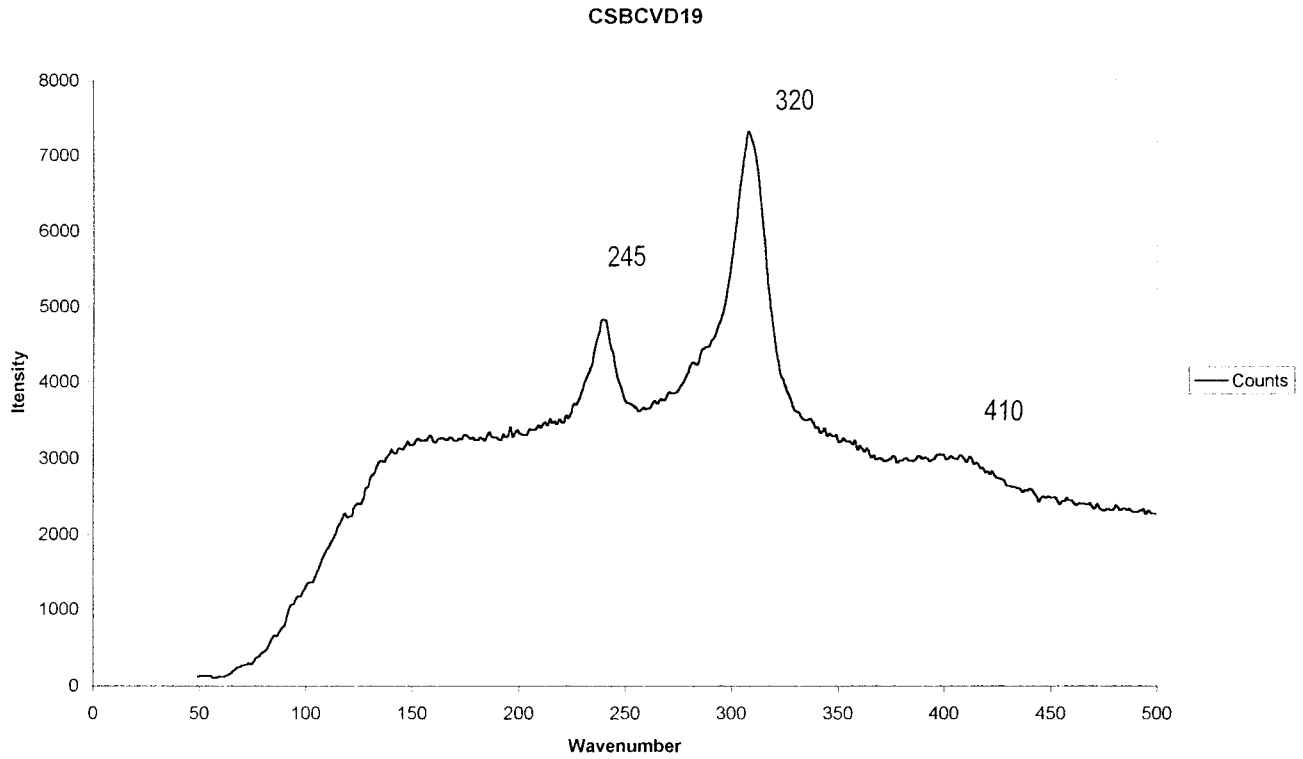

Figure 1. Raman spectra of the film formed from the APCVD of $TiCl_4$ and *t*-$BuPH_2$ at 550 °C.

1000 nm using a Helios double beam instrument. Reflectance and transmission spectra were recorded between 300 and 1200 nm by a Zeiss minature spectrometer. Measurements were standardized relative to a rhodium mirror (reflectance) and air (transmission). 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. Contact angle measurements of selected glass samples was determined by measuring the spread of a 7.5 μL droplet of water and applying a suitable program. Electrical conductivity was determined by four-probe measurement. Rutherford backscattering was obtained by Dr. Valizedeh at the University of Salford.

Photocatalytic potential of the samples was assessed by the destruction of an overlayer of stearic acid on a 4 cm × 4 cm portion of glass. This coated glass had been preirradiated at 254 nm for 1 h prior to measurement. The stearic acid was applied by dropping 7.5 μL of 0.004 M stearic acid onto the glass surface. The glass was spun at 1500 revolutions a minute during the dropping procedure. The IR spectra of the stearic acid overlayer was measured over the range 3000−2800 cm^{-1}. The stearic acid coated glass was irradiated at 15 min intervals for 1 h, using the 254 nm radiation provided by BDH germicidal lamps (2 × 8 W). Hardness scratch tests were conducted with felt pads, a brass stylus, and a stainless steel scalpel.

Caution! It should be noted that the dual source APCVD reaction of $TiCl_4$ and RPH_2 (R = *t*-Bu, Cy^{hex}, Ph) could conceivably proceed through a PH_3 intermediate. PH_3 is extremely toxic and can combine explosively with air. We have noted no adverse results to confirm this hypothesis in over 60 deposition experiments. However 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

Atmospheric pressure chemical vapor deposition (APCVD) of titanium phosphide films was achieved on glass substrates from the dual source CVD reaction of RPH_2 (R = *t*-Bu, Cy^{hex}, Ph) and $TiCl_4$. The process was studied at different substrate temperatures and flow rates of precursor (Table 1). No film could be grown at substrate temperatures below 400 °C. Uniform film coatings were obtained at 500 °C and above.

The films grown from the APCVD reaction of RPH_2 and $TiCl_4$ were silver in color at all substrate temperatures. On some occasions the leading edge (3 mm wide and the width of the substrate) of the films were a deep blue color. The films were highly optically reflective with the thickest films having a mirror like appearance. All of the films passed the Scotch brand tape test. The films were also free of pinhole and other defects. They could not be abraded with a felt cloth and could not be marked with a brass stylus. They could be marked with a steel scalpel. The films showed no change in visual appearance after storage in air for six months. They also showed no change in optical properties after several months immersion in common solvents (water, toluene, acetone) and dilute (2 M) mineral acids. Concentrated nitric acid and hydrochloric acids partly digested a film after 2 months immersion.

Raman microscopy was used to investigate all of the films. Raman patterns were obtained from the leading edge of the glass along the length of each coating. The Raman patterns were virtually identical at all points examined on the glass (Figure 1). This includes the pieces of glass that had a deep blue coloration. In all cases two main Raman bands were observed at 320 and 248 cm^{-1}. A weaker broad band was observed at 410 cm^{-1}. To our knowledge the Raman spectra of TiP has not been reported previously. Notably the Raman spectra of these thin films matched an authentic sample of bulk TiP prepared by solid-state metathesis.[8] It was noted that there was a slight shift in the Raman bands between the samples that were phosphorus-rich ($TiP_{1.14-1.29}$) and the fully stoichiometric samples TiP. In the fully stoichiometric case the Raman bands were noted at slightly lower frequency 306 and 242 cm^{-1}.

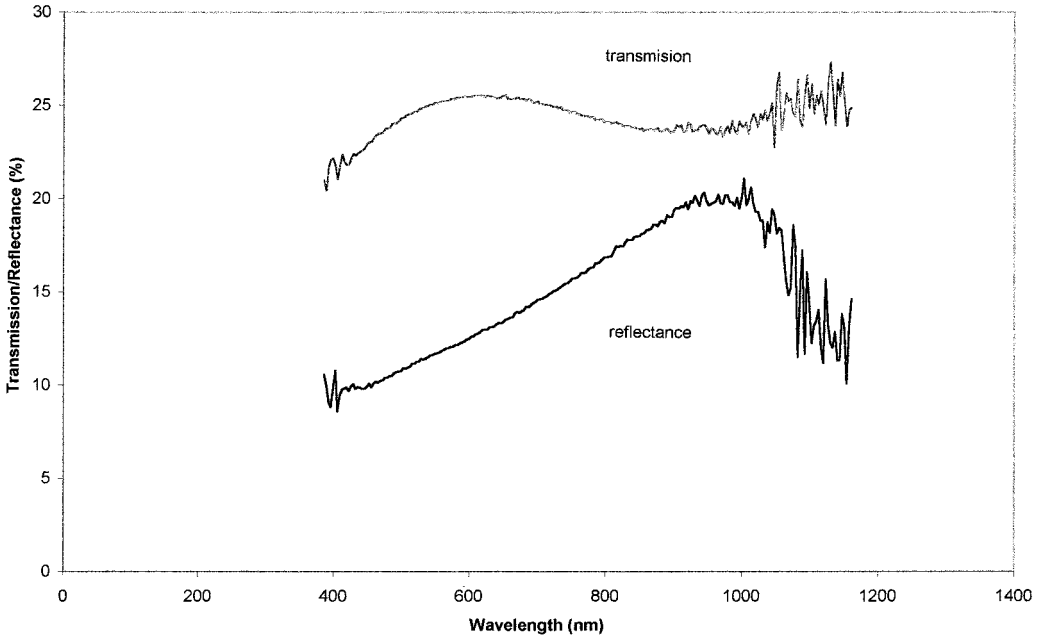

Figure 2. Reflectance/transmission spectra of (a) the product from the APCVD of $TiCl_4$ and *t*-$BuPH_2$ at 600 °C and (b) the product from the APCVD of $TiCl_4$ and *t*-$BuPH_2$ at 500 °C.

It was possible from the Raman analysis to focus on the very top layer of the samples. In some of the analysis of the APCVD reaction from $TiCl_4$ and $PhPH_2$ and $TiCl_4$ and Cy^{hex} a band attributable to anatase TiO_2 (143 cm^{-1}) was observed along with the titanium phosphide bands.[13]

Composition analysis of the films was determined by spot EDAX analysis and by electron probe line mapping. The EDAX results showed that the films were free of chlorine and showed only titanium and phosphorus. On some samples breakthorough to the underlying glass was observed. This was corrected for on the basis of a sample of plain glass. The EDAX analysis showed that only under one set of conditions was a fully stoichiometric TiP film obtained (Table 1); under all other CVD conditions, a slightly phosphorus-rich film was obtained. The electron probe line analysis allowed for line mapping over 1 cm portions of the films. The titanium-to-phosphorus ratios obtained from this analysis matched well with the EDAX results, in that in most cases a slightly phosphorus-rich film was observed. The line probe analysis showed that the films were fairly uniform with virtually no variation in the basic number of elemental counts. Chlorine was seen at detection limits (ca. 1% or less) in some films from the microprobe analysis. It was noted that the blue leading edge seen on some of the films had the same composition analysis as the remainder of the coating. Electron line probe analysis did show that at the extreme side edges of the coatings there was a slight variation in film composition, and a slightly higher amount of phosphorus was observed (ca. 10% excess over the main stoichiometry).

SEM analysis of the films showed that all of the films were uniform. The films were consistent with an island growth mechanism. Deposition rates were determined at ca. 1 μm min^{-1} for the reactions involving *t*-$BuPH_2$ and $Cy^{hex}PH_2$ at a substrate temperature of 550 °C. Film thickesses were determined by SEM measurements and by breakthrough count rate to the underlying glass from EDAX.

The optical properties of the films were studied by reflectance/transmission measurements and UV absorption from 400 to 1150 nm. All of the films showed a similar UV absorption profile in that they absorbed strongly at 365 and 1100 nm but had a relatively flat absorption profile between these extremes. The uncoated glass absorption edge starts at 330 nm. The strong absorption at 1100 nm is probably a consequence of the high reflectivity of the coating at longer wavelengths. The films show reasonable transmission of ca. 20−30% in the region 400−1000 nm (Figure 2). However, the thickest films grown at 600 °C showed minimal 5% transmission. The reflection profile of all of the films shows a characteristic pattern with strong reflectivity at 1000 nm.

XPS measurements were obtained for one sample from each of the APCVD reactions of RPH_2 (R = *t*-Bu, ^{cyc}Hex, Ph) and $TiCl_4$. All of these measurements showed that the surface had been partially oxidized (depth ca. 20 nm) and was predominatly TiO_2. Sputtering removed the oxide overlayer and revealed Ti $2p_{3/2}$ and P $2p_{1/2}$ binding energy shifts of 454.6 and 128.6 eV, respectively, for each of the samples. These are in good agreement with previous literature measurements on bulk TiP (Ti $2p_{3/2}$, 454.6 eV; P $2p_{1/2}$, 128.4 eV).[14] No chlorine contamination was seen by XPS analysis (1−2% detection limit) for any of the samples. Notably the oxygen concentration decreased with depth and was present at only trace levels after extensive depth profiling (150 nm from surface).

Rutherford backscattering (RBS) experiments were obtained on one sample prepared from the reaction of *t*-$BuPH_2$ and $TiCl_4$ at 550 °C. This showed that the top 15 nm of the surface consisted of TiO_2; the next layer (ca. 50 nm thick) had composition $TiP_{1.10}O_{0.20}$; the next

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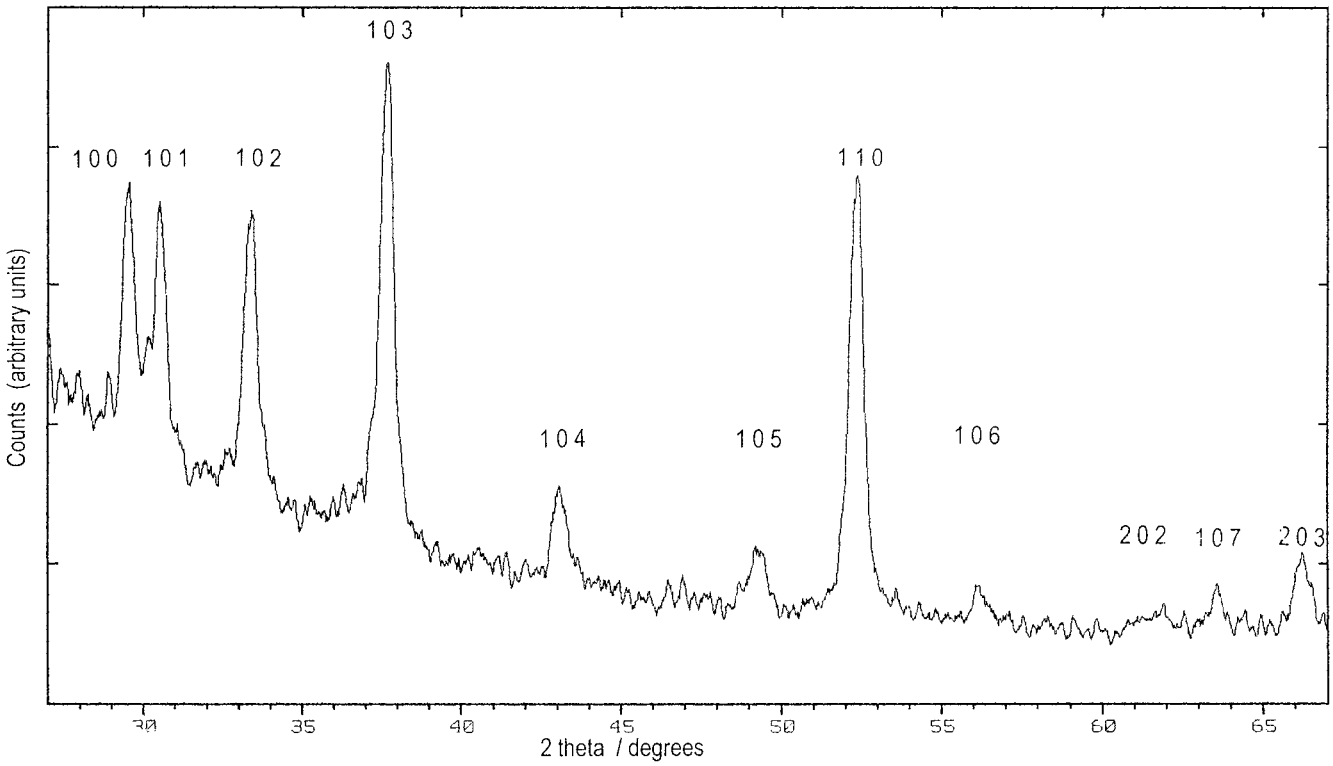

Figure 3. X-ray powder diffraction pattern of the film formed from the APCVD of $TiCl_4$ and *t*-$BuPH_2$ at 550 °C.

subsequent layer (ca. 50 nm thick) had composition $TiP_{1.15}O_{0.1}$. The bulk composition of the film (ca. 600 nm thick) was $TiP_{1.20}$. This indicates that titania covers the surface and that the degree of film oxidation is a function of depth. The bulk composition measurements matched well the EDAX measurements $TiP_{1.19}$, electron probe $TiP_{1.22}$, and sputtered XPS measurements, $TiP_{1.20}$ on the same sample. Notably, no chlorine was seen by the RBS technique.

The titanium phosphide films were crystalline. The film prepared at 550 °C with equal flows of $TiCl_4$ and *t*-$BuPH_2$ indexed with a hexagonal cell of $a = 3.49(1)$ Å and $c = 11.70(1)$ Å, (Figure 3). The films prepared from $TiCl_4$ and $Cy^{hex}PH_2$ and $PhPH_2$ also indexed with an equivalent hexagonal cell (R = Cy^{hex}, $a = 3.50(1)$ Å, $c = 11.71(1)$ Å; R = PhCy, $a = 3.50(1)$ Å, $c = 11.70(1)$ Å). This results compares favorably with bulk $TiP_{1.00}$; $a = 3.498(1)$ Å, $c = 11.70(1)$ Å for solid-state metathesis prepared material[6,7] and $a = 3.499(1)$ Å, $c = 11.700(6)$ Å from elemental combination reactions.[15]

The titanium phosphide films were shown to have contact angles of 40−50°. This contact angle did not change significantly on irradiation at 254 nm for 1 h. This contact angle is fairly similar to that observed on uncoated plain glass, 35−50°, indicating that the coatings are mildly hydrophobic. The titanium phosphide coatings show minimal activity as photocatalysts. They do partly degrade a stearic acid over layer when exposed to irradiation at 254 nm for 1 h. However the photodegradation is only around 10% after an hour's irradiation (uncoated glass showed a drop of 2% over the same time period).

The titanium phosphide coatings were conducting showing resistivities of 10−120 mΩ cm.

Discussion

Reaction of $TiCl_4$ and RPH_2 under APCVD conditions affords silver-colored films of titanium phosphide on glass substrates. The rate of film growth is comparable to that obtained in other APCVD systems involving $TiCl_4$.[16] The titanium phosphide films were shown in most cases to be rich in phosphorus, although at 550 °C when equal molar quantities of precursors were introduced in the gas-phase stoichiometric $TiP_{1.00}$ was obtained. The mechanism for the reaction was not determined in this study, although it is likely that HCl is produced in the reaction and that RCl and alkenes are also formed. Winter observed the formation of cyclohexene in a comparable LPCVD single-source study using $TiCl_4.(PH_2Cy^{hex})_2$. Notably the solution phase reaction of $TiCl_4$ and phosphines forms Lewis base adducts such as $[TiCl_4.(PR_3)_2]$. Winter et al.[10] and ourselves have shown that these adducts can form TiP coatings by low pressure CVD. Thus, it is probable that the APCVD reaction proceeds in its initial phase by formation of an adduct; indeed, some adduct was trapped and subsequently analyzed from the exhaust of the reactor. A potential mechanistic pathway is shown in Scheme 1.

The reactions were easiest to perform using *t*-$BuPH_2$, in that shorter deposition times (60 s typical) and lower phosphine bubbler temperatures were required. Equivalent thickness TiP coatings from reaction of $PPhH_2$ and $TiCl_4$ required a bubbler temperature of 100 °C, 180 s deposition time, and higher concentrations of the gas-

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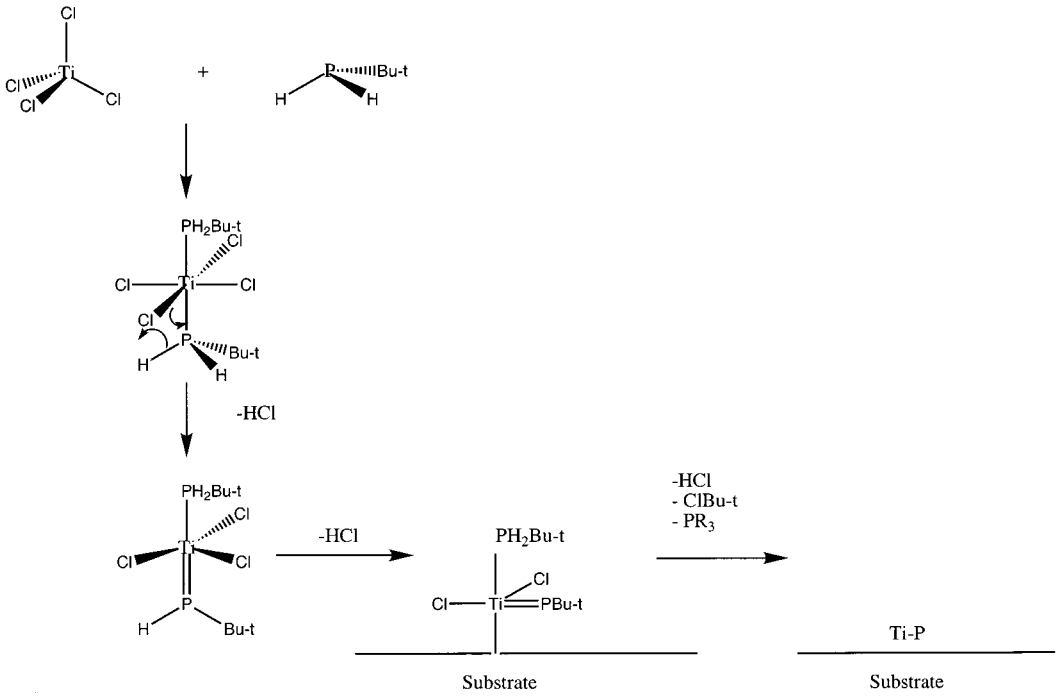
Scheme 1



eous precursors. Titanium phosphide coatings from reactions of $Cy^{hex}PH_2$ and $TiCl_4$ required a bubbler temperature of 130 °C, however equivalent thickness films were obtained to that of *t*-$BuPH_2$ in equivalent times. These results indicate that the nature of the R group does have a role in determining film growth rate.

A number of parameters changed with deposition temperature. The crystallinity of the films improved in each system with an increased in substrate temperature, as assessed by line broadening studies. The films were more electrically conducting when deposited at higher substrate temperatures with a resistivity of 10 mW cm for the film prepared from $TiCl_4$ and *t*-$BuPH_2$ at 550 °C. The concentration of the phosphine (*t*-$BuPH_2$, $Cyc^{hex}PH_2$) in the gas phase in each reaction had a baring on the film composition. In the *t*-$BuPH_2$ system, an increase in gas-phase concentration led to a more phosphorus-rich film (Table 1), from $TiP_{1.00}$ to $TiP_{1.29}$. Further, the amount of phosphorus seen in the films decreased with an increase in substrate temperature. Notably, despite these variations with reaction conditions, no film was obtained with a stoichiometry greater than $TiP_{1.3}$. This indicates that in formal oxidation state terms the films can be described as a mixture of Ti(III) and Ti(IV). The titanium(VI) films are favored at lower temperature and higher concentrations of the alkylphosphine precursor.

The titanium phosphide coatings grown by dual-source APCVD are very similar to those grown at low pressure using a single source approach. Winter has shown that a single-source approach works well for both TiP and NbP coatings on glass and silicon substrates.[10,11] Both sets of films were silver, reflective, and slightly rich in phosphorus, similar to the films reported here. One notable difference between Winters study and that reported here is that crystalline films could be readily obtained from the dual-source APCVD whereas from the single-source route the films gave diffuse diffraction patterns. This maybe due to the APCVD films being somewhat thicker than those from single-source deposition. Film growth rates are 2 orders of magnitude quicker in the APCVD technique.

The titanium phosphide coatings formed by APCVD have somewhat similar properties to that of titanium nitride formed from the APCVD of $TiCl_4$ and NH_3.[17] In both cases, an electrically conducting film was formed. Both sets of films are optically reflective, are conformal, cover the whole substrate, and are resistant to attack by common solvents and dilute mineral acids. The nitride films tended to be harder than the comparable phosphide films in that they could not be abraded with a steel scalpel. Both sets of films showed similar transmission and reflectance spectra, showing fairly good visible transmission (dependent on film thickness) but being highly reflective in the infrared. There was a notable difference in the color of the films formed by TiN and TiP. The TiN films formed by APCVD tended to be yellow or gold in color[16,17] while the TiP films were silver with in some cases a deep blue leading edge.

It was noted in the XPS, RBS, and Raman experiments that the surface of the TiP films had undergone some oxidation. On sputtering, the oxide layer could be removed and a TiP film obtained. It is probable that the surface layer consists of TiO_2. We have studied in some detail the APCVD of TiO_2 films on glass substrates. Formation of thin films of TiO_2 on glass give a very characteristic Raman pattern for anatase (143 cm^{-1}).[13] This was seen in some of the TiP films generated in this study. Thin films of anatase even at around 200−400 nm thickness become very hydrophilic on exposure to UV irradiation, giving contact angles below 5°. Notably the TiP films generated here are mildly hydrophobic with contact angles similar to the glass

(17) Hoffman, D. M. *Polyhedron* **1994**, *13*, 1169. Kurtz, S. R.; Gordon, R. G. *Thin Solid Films* **1986**, *140*, 277. Fix, R.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1991**, *3*, 1138. Musher, J. N.; Gordon, R. G. *J. Mater. Res.* **1996**, 989.

substrate. Further thin TiO_2 films (200 nm) are very photoactive in the destruction of an overlayer of stearic acid. The TiP films show only a small enhancement in photocatalytic activity above that of plain glass. This photoactivity is almost certainly a consequence of the thin 15−20 nm over coating of titania. The resistance of the TiP films formed in this study to acids and solvents as well as oxidation to air are a consequence of the overcoating TiO_2 layer. The overcoating TiO_2 layer is not formed directly in the CVD experiment as the bulk of the films have been shown to be largely free of oxygen by XPS, RBS, and EDX measurements. We believe that the oxide coating is formed on exposure of the sample to air. Furthermore, once formed the TiO_2 layer forms a barrier to further oxidation of the bulk of the material.

In some of the studies a deep blue material was formed at the leading edge of the silver TiP films. This edge was 3−4 mm wide and was analyzed separately. In both EDAX and Raman analysis, the blue edge of the film was identical to that of the silver portions of the film. Thin films of material formed by APCVD can often show a "rainbow-color" effect due to optical interference caused by variations in thickness. This was not evident in the TiP films. It is unlikely that the blue edge is caused by variations in film thickness because only a single color was observed. Further, shorter growth times and thinner films did not promote formation of an entirely blue film. Notably the blue film edge had reflectivity properties similar to the bulk of the film.

The reflectance/transmission spectra and the electrical properties of the films are similar to thin metal films. The films have some potential as solar control coatings. In this application a thin film of a material on a glass substrate needs to be transmitting in the visible region (400−800 nm) and reflecting in the IR (>800 nm). Such films can be used as windows and have the advantage of letting in solar radiation but reflecting back into the building the re-radiated IR energy. The silver and blue colors of the TiP films are favorable for use as solar control, coatings as they are visually appealing. Furthermore, the material is hard, is resistant to most chemicals, and, hence, has some potential both for exterior and interior window panes.

Conclusion

APCVD of $TiCl_4$ and RPH_2 (R = *t*-Bu, ^{cyc}Hex, Ph) at 450−550 °C form titanium phosphide films on glass substrates. The films show good surface coverage, adhesion and uniformity. The titanium phosphide films are silver, slightly phosphorus-rich, electrically conducting, and largely impervious to attack by common solvents. They are hydrophobic and largely unresponsive as photocatalysts. Reflectance spectra and electrical conductivity measurements indicate that the films have metallic properties.

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