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Dual source atmospheric pressure chemical vapour deposition of TiP films on glass using $TiCl_4$ and PH_2Bu^t

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A facile new method for the preparation of large area titanium phosphide films on glass is described from the atmospheric pressure chemical vapour deposition of titanium tetrachloride and *tert*-butylphosphine.

Thin films of early transition metal nitrides are widely studied and utilised by industry.[1] They have found application as diffusion barriers, hardness, wear resistant and solar control coatings.[2] Titanium nitride is the most important nitride for these applications combining the heat and electrical conductivities of metals with the refractory and brittle properties of ceramics.[3] Titanium nitride coatings have been synthesised from a range of single and dual source precursors.[4] Titanium phosphide coatings have, in contrast, seen very little exploration. This is surprising as TiP is refractory (dec. >1580 °C), hard, metallic and shows good resistance to oxidation even at elevated temperatures.[5] Bulk titanium phosphides have been characterised with a range of stoichiometries from Ti_3P through to TiP_2.[6] In bulk, TiP has been prepared by direct elemental combination[7] and, as reported by Kaner *et al.*, by solid state metathesis.[8] The TiP phase has a hexagonal structure consisting of alternating nickel arsenide and sodium chloride units. It was first prepared as a thin coating from a single source CVD by Winter *et al.*[9] They showed that adduct materials such as $Ti(PH_2C_6H_{11})_2Cl_4$ enabled growth of $TiP_{1.1}$ films on glass and silicon substrates at 400–600 °C by low pressure chemical vapour deposition. The materials gave diffuse X-ray patterns indicative of TiP rather than one of the other known TiP_x phases. The authors state that the single source route is eminently preferable because of control of film stoichiometry and the difficulties associated with dual source CVD.[9] Other routes to titanium phosphide coatings have been achieved from the reaction of phosphorus vapour on titanium plates at 650–900 °C (TiP–Ti_4P_3)[10] and from the reaction of $TiCl_4$, PCl_3 and H_2 at 900 °C.[11] Here we report the first dual source APCVD route to TiP coatings on glass from reaction of $TiCl_4$ and PH_2Bu^t. In particular the reactions are rapid and can be utilised to coat large areas of glass.

Reactions of $TiCl_4$ and PH_2Bu^t were studied under APCVD conditions at 350–600 °C. Films were grown on SiO_2 coated float-glass (9 × 3 cm) on a purpose built reactor.[12] The precursors were introduced into the gas stream by diverting the nitrogen carrier gases into heated bubblers. Precursor gas streams were mixed by a 1.5 cm concentric pipe before entering a mixing chamber prior to the reactor. No film could be grown in the system at substrate temperatures between 350 and 450 °C. Substrate temperatures of 500 °C and above produced silver mirror-like films that showed excellent surface coverage. The films were adhesive to the substrates, passed the Scotch tape test, could not be abraded with a cloth and were impervious to scratching with a brass scalpel. Chemically, the films showed no reactivity to water, common organic solvents and dilute mineral acids. Concentrated nitric acid partially digested a film after 48 h exposure.

Titanium phosphide films were characterised by a wide range of techniques. SEM showed that the films were uniform, and that growth rates were typically 1 μm min^{-1} at a deposition temperature of 600 °C. EDAX analysis over a number of surface spots indicated that any one film was homogeneous.† Films prepared at 600 °C were exactly stoichiometric TiP whilst the films prepared at 500 °C were slightly phosphorus rich $TiP_{1.1}$. The films showed negligible chlorine content by EDAX measurements (0–1%). XPS measurements showed that the surface had been partially oxidised (depth *ca.* 50 nm).‡ Sputtering removed the oxide over-layer and revealed Ti $2p_{3/2}$ and P $2P_{1/2}$ binding energy shifts of 454.6 eV and 128.6 eV respectively. 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).[13] No chlorine contamination was seen by XPS analysis (1–2% detection limit). The titanium phosphide films were crystalline and showed a glancing angle XRD spectrum for TiP, this indexed with a hexagonal cell; $a = 3.49(1)$ Å and $c = 11.70(1)$ Å.§ This compares favourably with bulk TiP; $a = 3.498(1)$ Å, $c = 11.70(1)$ Å for solid state metathesis prepared material[8] and $a = 3.499(1)$ Å, $c = 11.700(6)$ Å from elemental combination reactions.[14] The TiP films gave Raman spectra that matched bulk samples.¶ Optical properties of the films were measured. These showed that films of *ca.* 1 μm thickness had good transmission from 400–1200 nm (*ca.* 20–30%), however the films were highly reflective from 600–1100 nm. UV absorption spectra showed that the glass absorption edge is shifted from 330 nm to 375 nm and that the films are completely absorbing (reflecting) at 1070 nm and below. The films showed minimal photocatalytic activity in removing an over-layer of stearic acid. Hardness scratch tests showed that the films could not be marked with a brass stylus but could be scratched with a stainless steel scalpel.

The deposition of TiP films worked best at 550 and 600 °C. No films could be grown at 350 to 450 °C indicating that a specific temperature is required for the precursors to react to form a film. It is likely that the reaction proceeds by formation of a gas phase adduct $TiCl_4(PH_2Bu^t)_2$ which decomposes with loss of HCl and Bu^tCl to form TiP films. We have no evidence for the formation of this adduct, other than the colour of the particulate matter contained in the exhaust of the coater. Ourselves and Winter have shown separately that the simple adducts $TiCl_4 \cdot (PH_2R)_2$ will form TiP coatings in LPCVD experiments.[9,14] The dual source APCVD reaction has the advantage over the single source precursor approach in that the adduct does not need to be synthesised

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and the reaction can take place at atmospheric pressure without recourse to a vacuum system and leads to fast growth rates.

In summary, the dual source APCVD reaction of $TiCl_4$ and PH_2Bu^t offers a facile route to high quality TiP coatings on glass. The reactions give fast growth rates and can be readily adapted to coating large substrates from commercially available reagents. The ease of synthesis of these films by APCVD could open up a wide range of more sophisticated functional analysis.

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CAUTION! It should be noted that the dual source APCVD reaction of $TiCl_4$ and PH_2Bu^t 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 50 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.

Notes and references

[†] EDAX measurements were determined on a Jeol JSM820 microscope, equipped with a Kevex Quantum Delta 4 detector and standardised relative to polished elemental standards.

[‡] X-Ray photoelectron spectra were recorded with a VG ESCALAB 220i XL instrument using focussed (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.

[§] X-Ray powder diffraction patterns were measured on a Philips X-pert diffractometer using unfiltered Cu-Kα ($\lambda_1 = 1.5405$ Å, $\lambda_2 = 1.5443$ Å) radiation in the reflection mode using a glancing incident angle. Samples were indexed using Unit Cell.

[¶] 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.

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