Titanium phosphide coatings from the atmospheric pressure CVD reaction of $TiCl_4$ with PR_xH_{3-x} (R = Cy^{hex}; or R = $SiMe_3$ where x = 3)

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Transition metal phosphides form an interesting series of compounds with several potential applications. For example, the use of bulk powders for the catalysis of hydrodesulfurisation and hydrodenitrogenation reactions and as thin films in wear and corrosion resistant coatings and diffusion barriers in semiconductor devices.(1-3) However, the number of applications for the transition metal phosphides is extremely limited compared to the corresponding nitrides or the main group phosphides, which have been exhaustively studied.(4,5) Titanium (III) phosphide (TiP) is a hard, refractory metallic conductor, which shows good resistance to oxidation at elevated temperatures and has been suggested for use as a barrier coating for Al-W metallisation.(6,7) Previous routes to producing thin films of titanium phosphide have typically suffered from drawbacks, such as the use of highly toxic, pyrophoric phosphine (PH_3) gas or extremely high process temperatures.(7,8)

Here we report the APCVD reaction of $TiCl_4$ with primary, secondary and tertiary organophosphines (PR_xH_{3-x} (R = Cy^{hex})), and also with tristrimethylsilylphosphine ($P(SiMe_3)_3$.

The APCVD reaction of $TiCl_4$ with PR_xH_{3-x} (R = Cy^{hex}; or R = $SiMe_3$ where x = 3) leads to the deposition of titanium phosphide films in all cases. The films deposited using $Cy^{hex}PH_2$ were crystalline TiP. The use of $(Me_3Si)_3P$ also caused a thin film of crystalline TiP to be deposited. Reaction of $TiCl_4$ with the secondary and tertiary phosphines $Cy^{hex}{}_2PH$ and $Cy^{hex}{}_3P$ caused the deposition of thin films of titanium phosphide. However, oxidation of these films was significant and these phosphines are not considered to be suitable precursors for the deposition of titanium phosphide.

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