Precursor for the Low-Temperature Deposition of Titanium Phosphide Films

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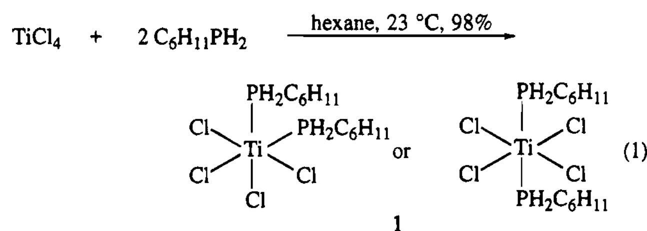
Received February 14, 1995
Revised Manuscript Received April 13, 1995

There has been little exploration of early transition metal phosphide materials, despite the favorable technological attributes of related MN (M = Ti, Al, Ga)[2a] and MP (M = Ga, In)[2b] phases. Monophosphides of the early transition metals are either metallic conductors (TiP, VP, NbP, TaP, and CrP) or superconductors (ZrP, HfP) and exhibit remarkable resistance toward oxidation.[3] Bulk titanium phosphide (TiP) is as hard as hardened high-carbon steel and decomposes at 1580 °C.[3a] TiP has a hexagonal B_i structure which consists of alternate units of sodium chloride (NaCl) and nickel arsenide (NiAs) structures.[4] Thin films of early-transition-metal phosphides have been used as diffusion barriers in semiconductor devices.[5] Sugiyama has reported the fabrication of TiP thin films by a chemical vapor deposition (CVD) route using the gas-phase reaction of titanium tetrachloride and phosphorous trichloride under hydrogen and argon atmosphere at 850–1050 °C.[6] Titanium phosphide film formation on titanium plates under phosphorous vapor at 650–900 °C was examined by Sasaki, although the composition of films varied between TiP and Ti_4P_3.[7] The high processing temperatures of the above-mentioned routes significantly restrict the choice of substrate in the film formation process. Recently, we reported the feasibility of using complexes $[TiCl_4(NH_3)_2]$[8] and $[TiCl_4(C_6H_{11}SH)_2]$[9] under low-pressure CVD conditions to obtain stoichiometric, high purity films of TiN and TiS_2 at low processing temperatures. Herein we report that the adduct derived from titanium tetrachloride and cyclohexylphosphine constitutes the first single-source precursor to high quality TiP films.

Treatment of titanium tetrachloride with 2 equiv of cyclohexylphosphine in hexane at ambient temperature, followed by evaporation of the solvent, afforded a spectroscopically pure yellow solid of $[TiCl_4(C_6H_{11}PH_2)_2]$ (**1**, 98%, eq 1). Sublimation of **1** (100 °C, 0.1 mmHg)

$$TiCl_4 + 2\,C_6H_{11}PH_2 \xrightarrow{\text{hexane, 23 °C, 98\%}}$$



yielded analytically pure, moisture-sensitive yellow crystals. Complex **1** was completely characterized by spectroscopic and analytical techniques.[10] The ^1H NMR spectrum of **1** showed a doublet of doublets for the P–H protons at δ 4.21 (J_{H-P} = 321 Hz, J_{H-H} = 5.1 Hz), as well as multiplets for the cyclohexyl hydrogens centered at δ 2.25, 2.17, and 1.81. The $^{31}P\{^1H\}$ NMR spectrum showed a single peak at −40.60 ppm (free ligand has a signal at −12.19 ppm). The infrared spectrum of **1** exhibited sharp P–H stretches at 2379 and 2376 cm^{-1}. For comparison, free cyclohexylphosphine showed a P–H stretch at 2282 cm^{-1}. The vapor pressure of **1** was 1–2 Torr at 25 °C, as determined by differential pressure measurements. This vapor pressure is very similar to that of the monomeric, octahedral adduct $[TiCl_4(C_6H_{11}SH)_2]$,[9] which implies that **1** is also a monomeric complex with either *cis*- or *trans*-phosphines. Tertiary phosphine complexes of the formula $[TiCl_4(PR_3)]$ and $[TiCl_4(PR_3)_2]$ are known,[11] although no X-ray crystal structures have been reported.

Fabrication of silver-colored titanium phosphide films from **1** was carried out under low pressure CVD conditions (dynamic vacuum, 0.1 mmHg) using a hot-walled tube reactor (quartz, 1 inch) within the temperature range 350–600 °C. Complex **1** was slowly sublimed (100 °C, 0.1 mmHg) into the hot zone containing glass (Corning 7059) or silicon substrates supported on a

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(10) Spectral and analytical data for 1: mp 119 °C (dec); IR (Nujol, cm^{-1}) 2379 (m) and 2376 (m, P–H stretches), 1293, (s), 1056 (s), 838 (s), 823 (s), 799 (s). ^1H NMR ($CDCl_3$, 23 °C, δ) 4.21 (dd, PH_2, J_{P-H} = 321 Hz, J_{H-H} = 5.1 Hz), 2.25 (m, $CHPH_2$), 2.17 (m, CH_2), 1.81 (m, CH_2), 1.71 (m, CH_2), 1.37 (m, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C, ppm) 33.06 (d, J_{P-C} = 4.3 Hz), 31.19 (d, J_{P-C} = 13.6 Hz), 26.66 (d, J_{P-C} = 9.2 Hz), 25.32 (s). ^{31}P NMR (CD_2Cl_2, 23 °C, ppm) −40.60. Anal. Calcd for $C_{12}H_{26}Cl_4P_2Ti$: C, 34.15; H, 6.21. Found: C, 33.90; H, 6.09. Despite numerous attempts, it was not possible to grow crystals of sufficient quality for an X-ray structure determination.

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ceramic stage. Passage of the vaporous precursor over the heated substrate resulted in titanium phosphide coatings. Deposition rates for films grown at 400 and 600 °C under these conditions were 480 and 300 Å min^{-1}, respectively.

X-ray photoelectron spectroscopy (XPS) of films made at 400, 500, and 600 °C divulged undetectable (≤2%) carbon or chlorine contamination. X-ray diffraction studies of films made at 350–600 °C showed a diffuse orientation and indicated the presence of a TiP phase and the absence of other possible compositions (Ti_4P_3, $Ti_{1.7}P$, and TiP_2).[12] Characterization using Rutherford backscattering spectroscopy (RBS) of a film made at 500 °C revealed a homogeneous composition throughout and a stoichiometry of $Ti_{1.0\pm0.05}P_{1.1\pm0.05}$. The absence of carbon or chlorine in RBS and XPS spectra indicates film purities of greater than 98%. The resistivities of films made at 400 and 600 °C were 286 and 421 $\mu\Omega$ cm, respectively. These values are slightly lower than the reported resistivity for bulk TiP (3400 $\mu\Omega$ cm).[2] The slight excess of phosphorus probably accounts for the lower resistivities in the films, relative to the bulk material. A scanning electron micrograph of a film made at 600 °C on Corning 7059 glass showed that the TiP consisted of flat, approximately hexagonal interpenetrating plates, with diameters of 600–1500 Å. A side view of the coated substrate revealed a dense film with complete coverage of the substrate.

The volatile products of a deposition carried out at 600 °C were collected in an NMR tube. A 10/30 joint was affixed to the NMR tube and the tube (cooled to −196 °C; containing 0.8 mL of chloroform-*d*) was then placed in an adapter situated at the end of the deposition tube.[13] The deposition system was evacuated to ca. 0.1 mmHg, and then the pyrolysis was conducted with the system isolated from the vacuum to allow efficient collection of the volatiles in the cold NMR tube. After collection, the tube was flame sealed and the sample was analyzed by a combination of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The major products were phosphine (35% of sample), hydrogen chloride (28% of sample), and cyclohexene (18% of sample).[14] Cyclohexene could be obtained by several paths, including β-hydrogen elimination from titanium-bound cyclohexylphosphine, abstraction of a hydrogen atom from a cyclohexyl radical, or elimination of phosphine from free cyclohexylphosphine. The phosphine could be produced on the metal center by loss of cyclohexene, followed by decomplexation. Alternatively, it could originate by elimination from free cyclohexylphosphine. The hydrogen chloride is obtained by phosphinolysis of the titanium–chlorine bonds. Minor products included cyclohexane (2% of sample), 1,3-butadiene (4% of sample), ethylene (2% of sample), and an unidentified C_7 or C_8 diene (11% of sample; structure proposed from analysis of 500 MHz ^1H NMR; its genesis is unclear). The 1,3-butadiene and ethylene probably result from a retro Diels–Alder reaction of cyclohexene.

In summary, $[TiCl_4(C_6H_{11}PH_2)_2]$ serves as the first single-source precursor to titanium phosphide films in the temperature range 350–600 °C. The availability of a low-temperature CVD process to TiP films should allow the properties and applications of this material and related metal phosphides to be explored. While the two-component atmospheric pressure CVD reaction of titanium tetrachloride and cyclohexylphosphine affords TiP films at ≥350 °C,[15] we prefer the single-source precursor approach outlined herein, due to the expense, toxicity, and exceptionally disagreeable odor of cyclohexylphosphine. Analogous alkylphosphine adducts of zirconium, hafnium, niobium, and tantalum halides have yielded phosphide phases under low-pressure CVD conditions.[16] The observation of hydrogen chloride as a byproduct of the deposition suggests that phosphido and phosphinidene complexes are intermediates in the film-forming process. We are studying the preparation of complexes bearing such linkages. These results will be published in due course.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9123339 to C.H.W.), Ford Motor Co., Glass Division, and the Institute for Manufacturing Research of Wayne State University, for financial support.

Supplementary Material Available: Experimental procedures and film characterization data (21 pages). Ordering information is given on any current masthead page.

CM950074N

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(14) These data should not be viewed as quantitative, since a portion of **1** always sublimed through the hot zone intact and because the geometry of the trap may not allow complete capture of the effluent products. Moreover, it is unknown what percentage of **1** actually decomposes to give the film, so the products could result from either the deposition process or a secondary gas-phase thermolysis. **Caution: The presence of phosphine in the reactor effluent requires efficient trapping, a well-ventilated reactor site, and extreme care when conducting film depositions.**

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