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Communications

Novel Nickel Precursors for Chemical Vapor Deposition

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From its very first attempt the focus of chemical vapor deposition (CVD) of nickel has been to replace the very toxic nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$, with a precursor that is less toxic.¹ $\text{Ni}(\text{cyclopentadienyl})_2$, $\text{Ni}(\text{methylcyclopentadienyl})_2$, $\text{Ni}(\text{ethylenediamine})(\text{hexafluoroacetylacetone})_2$, $\text{Ni}(\text{acetylacetone})_2$, $\text{Ni}(\text{hexafluoroacetylacetone})_2$, and $\text{Ni}(\text{diethylglyoximate})_2$ have been proposed as alternative precursors to deposit Ni with hydrogen as a reducing agent.^{2–13} Unfortunately,

the Ni films deposited from these precursors often exhibited significant incorporation of impurities such as oxygen and carbon, even when hydrogen was employed as a reducing agent. Although it was reported that $\text{Ni}(\text{diethylglyoximate})_2$ decomposed to produce pure nickel at a substrate temperature of 400 °C without H_2 , the breakdown of the ligands involved in thermal decomposition of the precursor is inherently prone to incorporating impurities in the deposited films. Due to its desirable properties, the nickelocene, $\text{Ni}(\text{cyclopentadienyl})_2$, has attracted much attention; however, the Ni films deposited from it exhibited high carbon contamination, limiting its use as a CVD precursor for deposition of high-quality Ni films.^{10–13}

Herein, we report new nickel(0) CVD precursors. Ever since it was first utilized for catalytic cyclization of propiolic acid esters, $\text{Ni}[\text{P}(\text{OEt})_3]_4$ has been known as a catalyst for the isomerization of olefins.^{14,15} In contrast to pyrophoric $\text{Ni}(\text{PEt}_3)_4$, $\text{Ni}[\text{P}(\text{OEt})_3]_4$ exhibited high thermal stability and low reactivity toward oxygen.¹⁶ The high stability of $\text{Ni}[\text{P}(\text{OEt})_3]_4$ is an attractive property as a CVD precursor. To be a viable CVD precursor, however, it should satisfy the volatility requirement as well. It was indeed shown that $\text{Ni}[\text{P}(\text{OEt})_3]_4$ is volatile and sublimable without thermal decomposition.¹⁷ We synthesized a series of tetrakis(trialkyl phosphite)nickel(0) complexes, $\text{Ni}[\text{P}(\text{OR})_3]_4$, where R = Me, Et, ³Pr, and Ph, and $\text{Ni}[\text{P}(\text{OR})(\text{OMe})_2]_4$, where R = Et, ³Pr, and ²Bu, which were isolated as volatile solids or liquids,¹⁷ and demonstrated the deposition of Ni using $\text{Ni}[\text{P}(\text{OMe})_3]_4$, $\text{Ni}[\text{P}(\text{OEt})_3]_4$, $\text{Ni}[\text{P}(\text{OEt})_3]_4$,

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$(OMe)_2$]₄, and $Ni[P(O^{\prime}Pr)(OMe)_2]$ ₄ as precursors at substrate temperatures as low as 200 °C without employing H_2 . The deposited films exhibited high purity and good surface morphology.

The homoalkyl phosphites, $P(OR)_3$, where $R = Me$, Et, $^{\prime}Pr$, and Ph, were purchased, and the heteroalkyl phosphites, $P(OR)(OMe)_2$, where $R = Et$, $^{\prime}Pr$, and $^{\prime\prime}Bu$, were prepared by modifying the literature method by the reaction of phosphorous trichloride with corresponding alcohols in diethyl ether.¹⁸ The nickel complexes were synthesized by adding the corresponding phosphite ligand to $NiCl_2 \cdot 6H_2O$ in methanol at 0 °C under N_2 followed by addition of diethylamine.^{16,19}

$P(OMe)_3$, $P(OEt)_3$, $P(O^{\prime}Pr)_3$, and $P(OEt)(OMe)_2$ gave sublimable solid nickel complexes while $P(OPh)_3$, $(O^{\prime}Pr)(OMe)_2$, and $P(O^{\prime\prime}Bu)(OMe)_2$ gave liquids. The sublimation temperature of the solid nickel complexes was elevated as the alkyl chain was lengthened.¹⁷ Both solid and liquid complexes were stable up to 170 °C except $Ni[P(O^{\prime}Pr)_3]$ ₄, which decomposed at 151 °C. The lower stability of the latter may be attributed to the steric bulkiness of the $P(O^{\prime}Pr)_3$ ligand. Among the liquid complexes, $Ni[P(O^{\prime}Pr)(OMe)_2]$ ₄ was distillable. These nickel complexes exhibited low reactivity toward oxygen.

CVD experiments were carried out in a cold-wall glass reactor with a bubbler-type precursor vessel that was maintained at 110 °C. Film depositions were conducted on Si(100) substrates at temperatures of 200–350 °C under reduced pressure of 0.5–1.0 Torr without employing H_2 . All the nickel complexes prepared in this study produced Ni films; however, in recognition of the higher stability and volatility, $Ni[P(OMe)_3]$ ₄, $Ni[P(OEt)_3]$ ₄, $Ni[P(OEt)(OMe)_2]$ ₄, and $Ni[P(O^{\prime}Pr)(OMe)_2]$ ₄ were selected herein as precursors to study the deposi-

(17) The NMR spectra were recorded in C_6D_6 on a VARIAN UNITY 400 NB NMR Spectrometer. $Ni[P(OMe)_3]$ ₄: solid (subl., 91 °C/0.05 Torr); 1H NMR (400 MHz) δ 3.57 (CH_3); ^{31}P NMR (161.903 MHz, C_6D_6 , H_3PO_4) δ 164.90. $Ni[P(OEt)_3]$ ₄: solid (subl., 96 °C/0.05 Torr); 1H NMR (400 MHz) δ 1.23 ($-CH_2CH_3$), 4.10 (CH_2); ^{31}P NMR (161.903 MHz, H_3PO_4) δ 160.38. $Ni[P(O^{\prime}Pr)_3]$ ₄: solid (subl., 112 °C/0.05 Torr); 1H NMR (400 MHz) δ 1.32 ($-CH_2CH_3$), 4.84 (CH); ^{31}P NMR (161.903 MHz, H_3PO_4) δ 156.62. $Ni[P(OPh)_3]$ ₄: liquid; 1H NMR (400 MHz) δ 6.60–7.35 (CH_6H_5); ^{31}P NMR (161.903 MHz, H_3PO_4) δ 154.20. $Ni[P(OEt)(OMe)_2]$ ₄: solid (subl., 94 °C/0.05 Torr); 1H NMR (400 MHz) δ 1.94 ($-CH_2CH_3$), 3.60 (CH_3), 4.10 (CH_2); ^{31}P NMR (161.903 MHz, H_3PO_4) δ 163.43, ^{13}C NMR (125.7 MHz) δ 58.3 (CH_2), 49.8 (CH_3), 16.7 ($-CH_2CH_3$); FAB Mass: 610.1 (M⁺), 472.1 (M– $P(OMe)_2(OEt)$), 334.0 (M–2 $P(OMe)_2(OEt)$), 196.0 (M–3 $P(OMe)_2(OEt)$). Anal. Calcd for $C_{16}H_{44}NiO_{12}P_4$: C, 31.45; H, 7.26. Found: C, 30.62; H, 7.25. $Ni[P(O^{\prime}Pr)(OMe)_2]$ ₄: liquid (b_p 180 °C/0.01 Torr); 1H NMR (400 MHz) δ 0.91 ($-CH_2CH_3$), 1.60 ($-CH_2CH_3$), 3.61 (CH_3), 3.97 (CH_2); ^{31}P NMR (161.903 MHz, H_3PO_4) δ 163.25; ^{13}C NMR (125.7 MHz) δ 64.2 (CH_2), 49.9 (CH_3), 24.5 ($-CH_2CH_3$), 10.7 ($-CH_2CH_3$); FAB Mass, 666.2 (M⁺), 514.1 (M– $P(OMe)_2(OPr)$), 362.0 (M–2 $P(OMe)_2(OPr)$), 210.0 (M–3 $P(OMe)_2(OPr)$). Anal. Calcd for $C_{20}H_{52}NiO_{12}P_4$: C, 36.00; H, 7.86. Found: C, 36.20; H, 7.96. $Ni[P(O^{\prime\prime}Bu)(OMe)_2]$ ₄: liquid; 1H NMR (400 MHz) δ 0.89 ($-CH_2CH_3$), 1.41, 1.60 ($-CH_2CH_2CH_3$), 3.62 (CH_3), 4.03 ($-OCH_2$); ^{31}P NMR (161.903 MHz, H_3PO_4) δ 163.86; ^{13}C NMR (125.7 MHz) δ 62.3 (CH_2), 49.9 (CH_3), 33.4 ($-CH_2CH_3$), 19.5 ($-CH_2CH_3$), 14.0 ($-CH_2CH_3$); FAB Mass 722.2 (M⁺), 556.2 (M– $P(OMe)_2(OBu)$), 390.1 (M–2 $P(OMe)_2(OBu)$), 223.0 (M–3 $P(OMe)_2(OBu)$). Anal. Calcd for $C_{24}H_{60}NiO_{12}P_4$: C, 39.85; H, 8.36. Found: C, 40.08; H, 8.57.

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(19) The nickel(0) compounds were prepared according to the method of ref 16. $P(OR)(OMe)_2$ (0.105 mol) was added dropwise to $NiCl_2 \cdot 6H_2O$ (5.0 g, 0.021 mol) dissolved in 100 mL of methanol at 0 °C. With further cooling and vigorous stirring, Et_2NH was added dropwise until the color of the solution changed to pink. Solid products were filtered and washed with cold methanol followed by drying under vacuum at room temperature. For the liquid products, the solvent was removed under vacuum and the residue was extracted with THF. The extracts were concentrated and eluted through neutral alumina. The product was isolated by removing the solvent and free phosphite under vacuum.

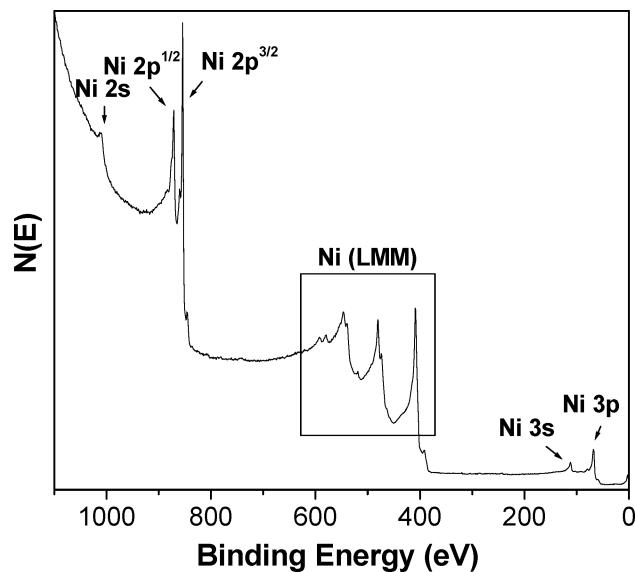


Figure 1. XPS spectrum of a Ni film deposited from $Ni[P(O^{\prime}Pr)(OMe)_2]$ ₄ at 200 °C on Si.

tion behavior. The precursor was injected upward into the reactor with argon as a carrier gas at two flow rates, 300 and 600 sccm. The precursor feed and reaction pressure were controlled by the carrier gas flow rate during the deposition processes. Higher argon flow would therefore lead to higher precursor feed and higher reaction pressure, and vice versa. The deposited Ni films were analyzed by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM).²⁰

The deposited Ni films exhibited high purity. Adhesion of the films to the substrate was good. Neither gas-phase reactions nor deposition of nickel on the reactor wall was observed during the deposition process. The high thermal stability of the new precursors could be attributed to this. Figure 1 shows an XPS spectrum of a Ni film deposited from $Ni[P(O^{\prime}Pr)(OMe)_2]$ ₄ on Si at 200 °C after etching the film with argon ion for 1 min with a sputtering rate of 30 Å/min. Before the film was etched, the peaks for the carbon and oxygen species were observed along with those for the elemental nickel; however, as shown in Figure 1 the former species disappeared after etching whereas the latter remained in the film. Phosphorus contaminants were not detected from the film. This indicated that the carbon and oxygen contaminants were present only at the surface that was exposed to the ambience after the deposition process and that the film deposited from the precursor was pure nickel. Since hydrogen was essential to reduce the carbon incorporation in the Ni films produced from the conventional precursors such as nickel acetylacetones or nickelocenes, it is remarkable that pure Ni films could be deposited from the present precursors in the absence of hydrogen. Indeed, it was reported that carbon incorporation in the Ni films deposited from nickelocene increased with a decrease in the hydrogen flow rate whereas

(20) XPS spectra were obtained by using a Physical Electronics PHI 5400 X-ray photoelectron spectrometer with a monochromatized $Mg K\alpha$ X-ray source (1253.6 eV). All the films were cleaned extensively by sputtering with argon at 8 keV before data collection. SEM and AFM images were taken from a Hitachi S-4700 scanning electron microscope and a Digital Instruments Multimode NanoScope IIIa, respectively.

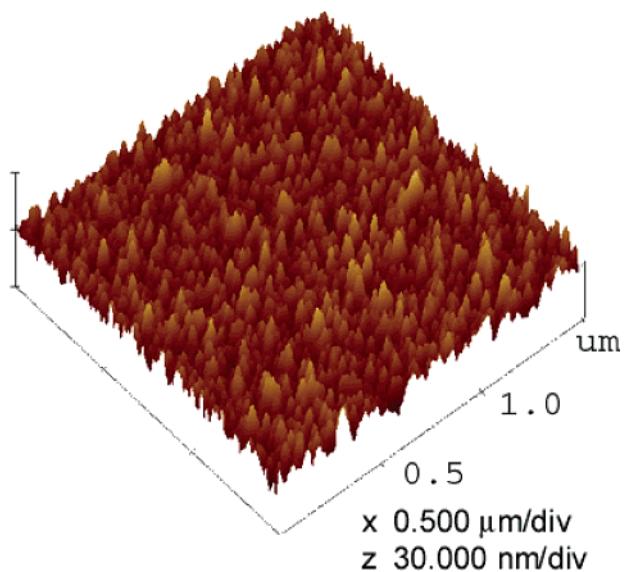


Figure 2. AFM image of a Ni film deposited from $\text{Ni}[\text{P}(\text{O}'\text{Pr})(\text{OMe})_2]_4$ at 200 °C on Si.

nickel deposition was not possible at temperatures lower than 550 °C in the absence of hydrogen.^{2,10–13} To study the decomposition behavior of the precursors during the deposition process, the exhaust gas from the CVD reactor was collected for each precursor in a liquid nitrogen trap and analyzed by ^1H NMR. This analysis indicated that the exhaust was the corresponding trialkyl phosphite ligand liberated from the precursor molecule intact, which lends support to the high purity of the deposited Ni films. The Ni films deposited from the present precursors were smooth and dense. The rms surface roughness of the films measured by AFM ranged between 3.19 and 4.62 nm. Figure 2 shows an AFM image of the film used for the XPS analysis in Figure 1, illustrating the smooth and dense film morphology. The rms roughness of the film was 3.53 nm.

The film growth rate increased with the substrate temperature and precursor feed under the processing

conditions used in this experiment. A typical film growth rate for $\text{Ni}[\text{P}(\text{O}'\text{Pr})(\text{OMe})_2]_4$ was 80 Å/min at 200 °C with an argon flow rate of 300 sccm. The film growth rate increased to 90 Å/min as the temperature was raised from 200 to 250 °C or the argon flow rate from 300 to 600 sccm with the rest of the parameters unchanged in either case. Figure 3 shows the SEM images of the Ni films deposited from $\text{Ni}[\text{P}(\text{OMe})_3]_4$ and $\text{Ni}[\text{P}(\text{OEt})_3]_4$ and Figure 4 those from $\text{Ni}[\text{P}(\text{OEt})(\text{OMe})_2]_4$ and $\text{Ni}[\text{P}(\text{O}'\text{Pr})(\text{OMe})_2]_4$ at substrate temperatures of 200 and 250 °C and argon flow rates of 300 and 600 sccm. It was interesting to observe that the effect of the substrate temperature and argon flow rate on the grain growth and morphology of the deposited films varied with each precursor. When $\text{Ni}[\text{P}(\text{OMe})_3]_4$ was used as a precursor, the effect of the precursor feed on the grain growth was significant while that of the substrate temperature was negligible. The opposite was observed for the films deposited from $\text{Ni}[\text{P}(\text{OEt})(\text{OMe})_2]_4$, where the effect of the substrate temperature was more prominent. On the other hand, neither the substrate temperature nor the precursor feed rate seemed to affect the grain growth for the films deposited from $\text{Ni}[\text{P}(\text{OEt})_3]_4$. More detailed studies on the deposition mechanism are needed to understand the seemingly different behaviors of the precursors during the film growths.

In this report, we presented a number of nickel(0) complexes that may serve as new CVD precursors for depositing high-quality Ni films. These new precursors have the following promising properties: (1) They are volatile and exhibit high thermal stability and low oxygen sensitivity; (2) they produce dense, smooth, and high-purity Ni films at low substrate temperatures without hydrogen; (3) they exhibit neither gas-phase reactions nor thermal decomposition of the ligands dissociated from the precursor molecule during the deposition processes; (4) $\text{Ni}[\text{P}(\text{O}'\text{Pr})(\text{OMe})_2]_4$ is available as a distillable liquid, making them even more attractive for practical CVD processes.

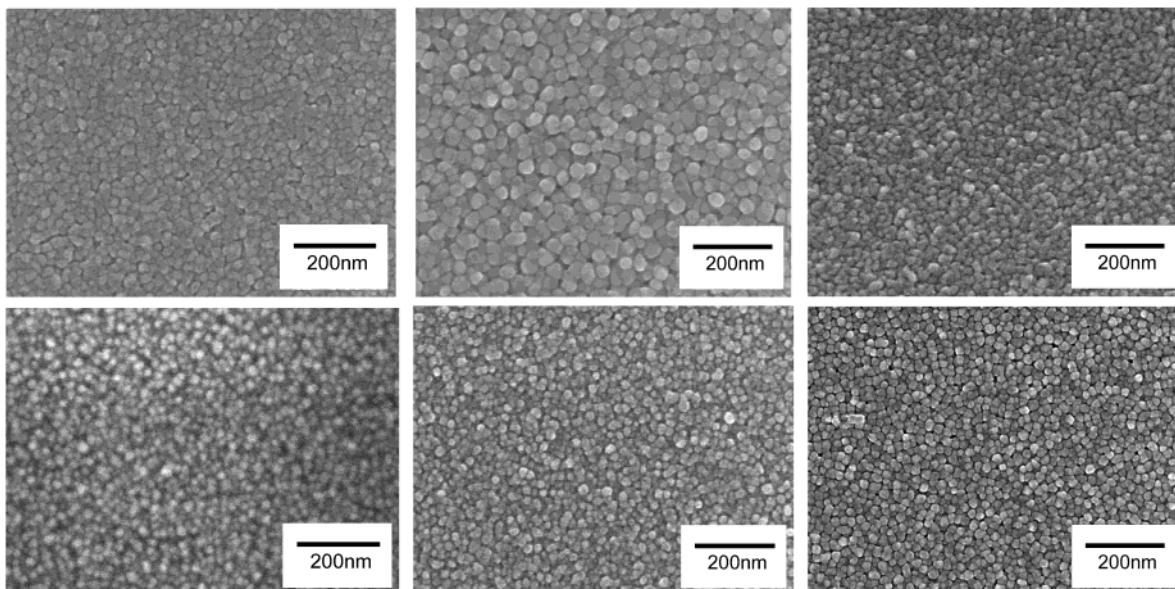


Figure 3. SEM images of Ni films on Si, deposited from $\text{Ni}[\text{P}(\text{OMe})_3]_4$ (top) and $\text{Ni}[\text{P}(\text{OEt})_3]_4$ (bottom). Deposition temperature and Ar flow rate are from left to right: 200 °C with Ar flow rate of 300 sccm, 200 °C with Ar flow rate of 600 sccm, and 250 °C with Ar flow rate of 300 sccm.

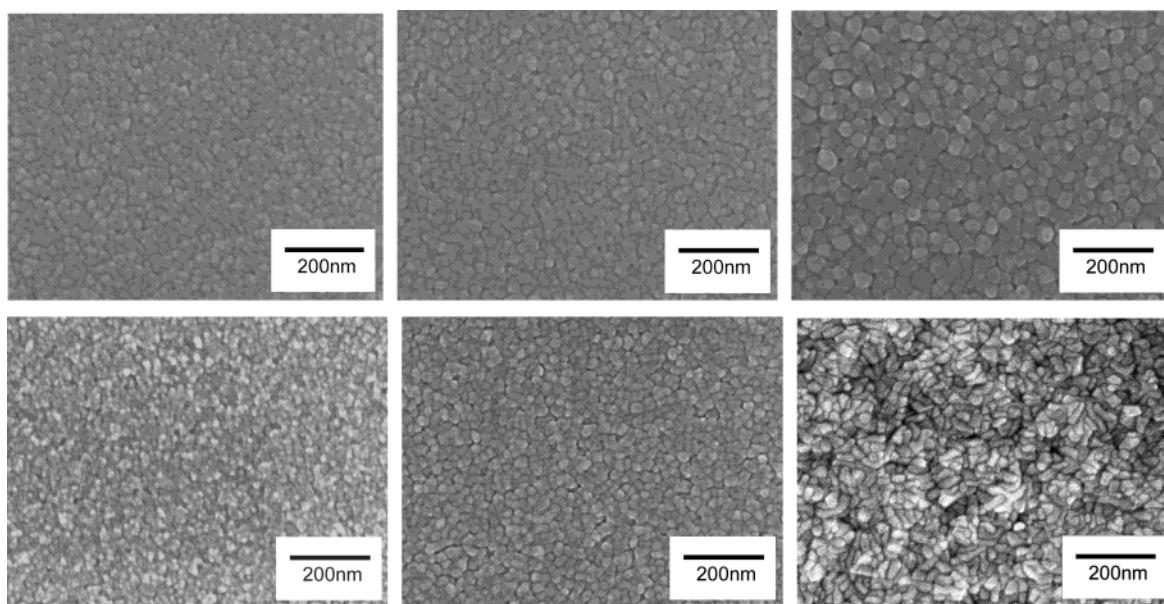


Figure 4. SEM images of Ni films on Si, deposited from $\text{Ni}[\text{P}(\text{OEt})(\text{OMe})_2]_4$ (top) and $\text{Ni}[\text{P}(\text{O}'\text{Pr})(\text{OMe})_2]_4$ (bottom). Deposition temperature and Ar flow rate are from left to right: 200 °C with Ar flow rate of 300 sccm, 200 °C with Ar flow rate of 600 sccm, and 250 °C with Ar flow rate of 300 sccm.

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