Preparation of a Plasma Polymer Containing Phosphine Complexed Nickel by Concurrent Nickel Evaporation

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SYNOPSIS

This article describes one of the first examples of concurrent metal evaporation and substituted hydrocarbon plasma polymerization as a general method for preparing thin films containing a metal coordinated to a plasma polymer. In this report, the evaporation of Ni into a triallylphosphine (TAP) glow discharge is described. Deposition of a plasma polymer with concurrent reaction of Ni atoms with phosphine groups forms nickel containing triallylphosphine plasma polymer, NiTAPPP. The chemical nature of the product is derived on the basis of infrared spectra taken of the film as formed and after reaction with air, CO, and NO. The extent of the reaction is deduced from gravimetric data obtained during reaction with CO and with NO; each case was followed by evacuation of the gas. The CO gravimetric data also suggest that uncoordinated Ni is predominantly formed at high (Ni evaporation rate)/(plasma polymer deposition rate) ratios; coordinated Ni predominates at low values of this parameter. The ESCA spectra are also obtained for this plasma polymer (NiTAPPP) as well as for that described in the previous paper, in which TAP is plasma polymerized (yielding TAPPP) and subsequently reacted with Ni(CO)$_4$ (TAPPP + Ni(CO)$_4$). In both cases, it was found that Ni is oxidized on contact with air. After such air exposure, ESCA spectra reveal the presence of residual Ni—P moieties on the surface of TAPPP + Ni(CO)$_4$, but not of NiTAPPP. This is attributed to the greater reactivity of the coordinatively unsaturated Ni sites postulated for NiTAPPP.

INTRODUCTION

The preparation of plasma polymers, in which metal atoms are complexed by functional groups attached to the plasma polymer network, has been our goal for a number of years. In a previous publication, we briefly reviewed various methods of attaining this goal and our results thus far.[1,2] We demonstrated that triallylphosphine (TAP) can be plasma polymerized to form an insoluble film (TAPPP) with retention of reactive and accessible phosphine groups.[1] The presence of these groups was demonstrated gravimetrically and by the use of infrared spectroscopy before and after reaction with selected reagents.

In this article, we present results showing that a plasma polymer containing Ni atoms complexed to phosphine groups can be prepared by combined Ni evaporation and TAP plasma polymerization. The same techniques used previously[1] are employed to support this assertion; ESCA spectroscopic data are presented as well. The Ni containing plasma polymer (NiTAPPP) was reacted with O$_2$ (air), CO, and NO. It has been demonstrated that the agglomeration of evaporated metal atoms into aerosol particles can be retarded and chemical bonds can be formed by the presence of a plasma.[3]

The incorporation of a phosphine in conventional polymers has been studied since the early 1970s.[4] The advantage of this phosphorus modification is in the ability of the phosphorus atom to act as a ligand in metal complexes. Rapid growth in the area

of phosphorus derivatized polymer supports occurred, in part, because of researchers who have attempted to immobilize homogeneous catalysts. This modification yields increased reactivity and selectivity over normal heterogeneous catalysts, and simpler separation and recycling of catalysts as compared to homogeneous catalysts.[5]

Phosphorus modification of polymers has traditionally been accomplished using two methods. Either the polymer was treated with a phosphorylating agent, or the monomer was phosphorylated and then polymerized.[6] The most common modification is the phosphorylation of polystyrene. The phosphorus modified polymer films have been used to coordinate several different metal complexes (e.g., Rh, Pt, and Ni) with varying degrees of success.[7]

The stability of the traditional phosphorus modified polymers is questioned in results reported by Garrou.[8] The lack of stability could possibly be a result of the method of phosphorus modification. The phosphorus is usually bound to the polymer backbone by a single P–C bond. It appears that with certain homogeneous catalysts, this bond can be broken at relatively low temperatures (100°C).[9] This leads to the undesirable result that immobilized catalyst is lost to the solution. The TAPPP described here binds the phosphorus through an unspecified

number of P–C bonds (up to 3, as in the monomer) and thus the phosphine might be expected to show greater stability than it does when found in conventional polymer systems. Additionally, plasma polymers, as described here, can be routinely formed as thin films of thickness 50 nm–500 nm. Such thin films have advantages for applications involving mass transport phenomena, such as surface modifications of electrodes for electrochemistry, and for applications involving surface phenomena, such as catalysis.

EXPERIMENTAL

Materials

Nickel metal (99.9% pure) for evaporation was obtained from Fisher Scientific. The ethane employed as a comonomer to form nickel ethane plasma polymers was used as obtained from Airco Inc. Other reagents and materials are identical to those described elsewhere.[1]

NiTAPPP Plasma Codeposit Production

The formation of a NiTAPPP codeposit was accomplished by combining the plasma polymerization of
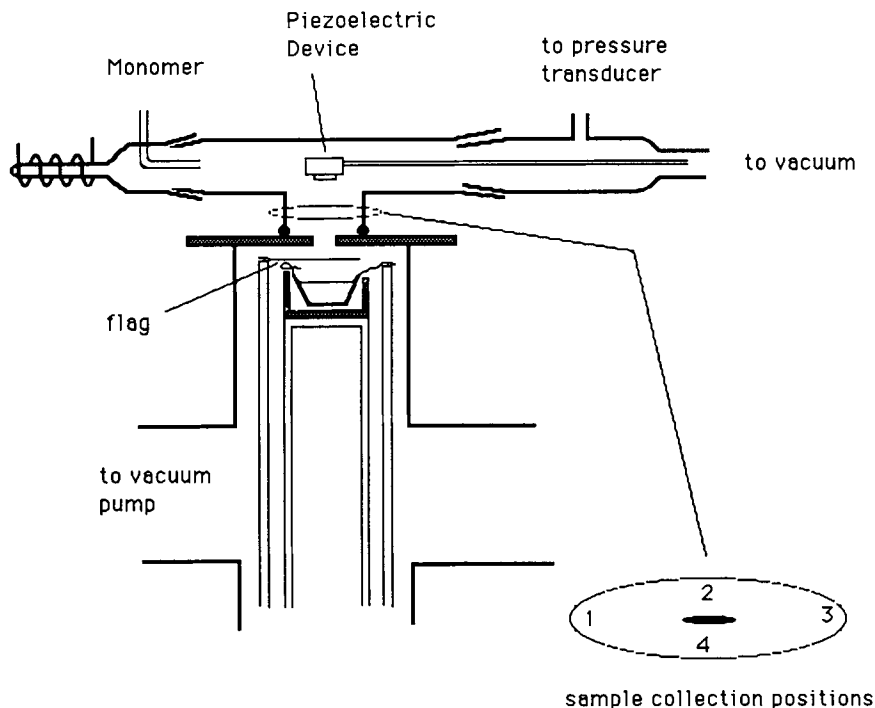

Figure 1   Schematic diagram of the crucible and reaction chamber for the production of NiTAPPP. The insert indicates the position of substrates in the reactor, as viewed from the top.

TAP[1] with evaporation of Ni metal into the reactor. Figure 1 is a schematic representation of the reactor used for the codeposition process. The reaction chamber used in our previous study[1] was modified by addition of a "T" fitting, 5.0 cm inside diameter (i.d.) and 4.5 cm long. This fitting is sealed to the aluminum bulkhead of a glass cross, 6 in. i.d., using an O-ring fitting. Nickel is evaporated from a crucible contained within the glass cross; it reaches the reactor through a 4 mm i.d. hole in a 0.2 mm thick molybdenum sheet separating the two chambers. The conical crucible is made of a spiral, 1.4 mm diameter molybdenum wire, covered with a cured alumina cement.[10] The crucible, 2 cm deep, is situated with the plane of its top rim 1.3 cm below the molybdenum sheet and is charged with 6 grams of Ni. A horizontal molybdenum flag blocks the flow of evaporating metal to the reactor when it is positioned over the crucible; removal of the flag allows instant initiation of metal atom flux to the reactor at a predetermined rate. NiTAPPP was collected on aluminum or glass blanks. These were placed on the wall of the "T" portion of the reactor at a height of 2 cm from the surface of the bulkhead at azimuthal positions 1, 2, 3, and 4, as depicted in Figure 1. Alternatively, NiTAPPP was deposited on the piezoelectric crystal of a deposition rate monitor placed on the roof of the reactor directly above the crucible, as described below. Because samples were collected at different locations, the *in situ* gravimetric data, obtained for a given experiment, described a different sample from that used, for example, for infrared analysis. Generally, the deposition rate monitor deposited films had the higher metal loading.

The procedure for the preparation of a NiTAPPP film is as follows: The delivery rate of Ni to the reactor is first set. This is accomplished by increasing the current through the crucible until the desired delivery rate is obtained, as measured by a deposition rate monitor (Inficon Model XTM) positioned at the top surface of the reactor directly over the entry point for the metal. The delivery rate is set with the pressure in the reactor and glass cross below 1 mTorr. Under these conditions, delivery of metal is by straight-line translation from the crucible through the hole at the bottom of the "T" portion of the reactor to the roof of the reactor; a conical "beam" of metal flux is observed. There is, therefore, no metal deposition on the walls of the "T" portion of the reactor. The flag is now positioned over the crucible to shut off metal flux to the reactor. TAP is introduced into the reactor at the desired flow rate and pressure; the glow discharge is initiated. The flag is then displaced to allow metal evaporation

into the plasma. It should be noted that the plasma pressure is typically 4–6 mTorr; the pressure in the bulk of the glass cross remains below 1 mTorr. Under these conditions, metal deposition occurs on the walls of the "T" portion of the reactor, even in the absence of plasma or of TAP (e.g., in 4–6 mTorr of Ar gas). This deposition is caused by scattering of the metal beam by collisions of metal atoms with gas molecules. The glow discharge is started 20 sec before the flag is opened, and is stopped 2 sec before the flag is closed. NiTAPPP was maintained under vacuum for an additional 3 h before exposure to the atmosphere. The nickel deposition at the four positions was measured gravimetrically by weighing aluminum foil and glass substrates before and after deposition. The resulting codeposition product was monitored by IR, x-ray photoelectron (ESCA), and atomic absorption spectroscopies.

For a given metal evaporation rate, the plasma polymer codeposition rate at a given site in the reactor was constant to $\pm 15\%$ for over 20 replicate runs. We conclude that the nickel content falls within these tolerances.

NiEthPP Plasma Codeposit Production

A nickel-containing plasma polymer was made by combining the evaporation of nickel metal with the plasma polymerization of ethane. This plasma polymer (NiEthPP) was fabricated in a manner similar to NiTAPPP with the substitution of ethane for TAP. A flow rate of 0.29 cc/min ethane ($P_m = 3.8$ mTorr) into the reaction chamber resulted in $P_g = 4.2$ mTorr. The plasma polymer was used as a preparation, in which no complexing of nickel to the plasma polymer was expected to aid in interpreting the ESCA results for NiTAPPP.

Mass Gain

Experiments measuring the mass gain of thin films of NiTAPPP, when exposed to reactive gases, were carried out, using an Inficon Model XTM deposition rate monitor and a gold plated crystal. NiTAPPP codeposits were exposed to 0.160 atm. of CO, NO, or O_2 for a period of time. The mass of the film was monitored continuously, by means of a strip chart recorder, during the addition and removal of the gases.

Spectroscopic Characterization of Plasma Polymers

Infrared spectra were obtained without exposure to the atmosphere as described previously.[1] Spectral

Table I   Reactor Conditions for Plasma Polymerization[a]

Film	P_m (mTorr)	P_g (mTorr)	TAP Flow Rate (cm^3 min^{-1})	R. F. Power (watts)	Deposition Rate[b] (μg cm^{-2} min^{-1})
TAPPP	6–10	3	0.014–0.016	8–10	0.75
NiTAPPP[c]	6–12	3	0.014–0.016	8–15	1.25

[a] Samples were prepared using the reactor shown in Figure 1.

[b] At position 2 of reactor (see Fig. 1), 2 cm from reactor bottom.

[c] Ni evaporation of approximately 2.00 μg cm^{-2} min^{-1}.

characterization of plasma polymer films was based on six replicate spectra. All absorption bands used for characterization were reproducibly obtained at precisely the same position for each replicate experiment. ESCA (electron spectroscopy for chemical analysis) spectra were obtained after exposure to air using a Physical Electronics Phi Model 548 ESCA spectrometer equipped with Mg K-alpha X-ray source, equipped with a model 15–255 precision electron energy analyzer. Plasma polymer was deposited on aluminum foil blanks. ESCA spectra were obtained within 24 h of sample preparation for TAPPP exposed to CO, 24–48 h for NiEthPP, and 72–96 h for NiTAPPP. A correction for charging was made by reference to the major contributor to the C 1s line at 284.6 eV (aliphatic carbon). The relative amount of each element was obtained from the ESCA signal using sensitivity factors supplied by the instrument manufacturer. The O 1s, C 1s, P 2p, and Ni $2_{p3/2}$ peaks were resolved into spectral peaks representing various functional groups of molecules using a computer program by Smith,[11] assuming a Gaussian–Lorentzian fraction of 0.4.

Reactions of NiTAPP Plasma Polymer Film with CO and NO

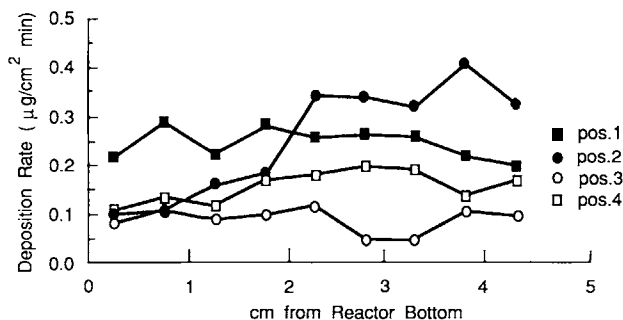The reaction of NiTAPPP with the reactive gases, CO and NO, was followed gravimetrically and by

Figure 2 Nickel deposition rate as a function of location in the reactor at sample collection positions, as defined in Figure 1.

infrared spectroscopy in a manner similar to that described for TAPPP previously.[1] The only deviation from that procedure lay in the exposure of NiTAPPP samples to air for 2 min while transferring the reactor from atop the glass cross to the N_2 purged glove bag. As before, the aluminum foil was transferred inside a glove bag to the ATR accessory for examination by IR spectroscopy.

RESULTS

Nickel Containing Triallylphosphine Plasma Polymer (NiTAPPP)

Deposition rates for TAPPP and NiTAPPP are given in Table I along with experimental conditions. The incorporation of Ni in TAPPP resulted in a modification of the TAPPP deposition rate. The modification of this rate was due to the inclusion of Ni in the film, which was confirmed using a dimethylglyoxime spot test. More insight into the nature of the deposition process was obtained from a quantitative analysis of %Ni composition, obtained by atomic absorption spectroscopy in comparison to NiTAPPP and TAPPP deposition rates.

The distribution of Ni deposition rates on the wall of the "T" portion of the reactor, as a function of distance from the bottom surface, is shown in Figure 2 for Ni evaporation into 5 mTorr of Ar. The difference in deposition rates on the walls of the reactor as a function of azimuthal position is caused by several factors. These include lack of centering of the entry hole for Ni with regard to the cylindrical axis of the "T" portion of the reactor and the conical axis of the crucible, as well as lack of perfect verticality for the crucible's conical axis.

The mass %Ni content of NiTAPPP samples obtained analytically is given in Table II. Here the deposition rate for NiTAPPP is measured for a series of aluminum foil blanks, placed at incremental heights at azimuthal positions 1 and 2 on the walls of the "T" portion of the reactor. The %Ni content,

Table II   Mass Percent Ni Obtained from Atomic Absorption Spectroscopy along with an Estimated %Ni in NiTAPPP Obtained by Subtraction of TAPPP Deposition Rate Values from Deposition Rate Values of NiTAPPP

Sample Position[a] (cm from the Reactor Bottom)	%Nickel[b]		Estimated %Ni[c]	
	Pos. 1	Pos. 2	Pos. 1	Pos. 2
4.25			32	42.7
3.75			32.6	44.9
3.45	20.4	9.47		
3.25			28.8	42.1
2.75			37.1	45.0
2.25			41.9	49.9
1.85	11.6	8.52		
1.75			45.2	46.6
1.25			44.9	49.2
0.75			40.9	46.9
0.25	7.01	—	41.5	44.8

[a] Samples were obtained from position 1 and 2, shown in Figure 1. The distance is measured from the metal plate separating the metal chamber from the reaction chamber.
[b] %Ni values obtained by A. A. spectroscopy of samples coated on glass coverslips. Atomic absorption spectroscopy results obtained by D. Binstock at RTI.
[c] %Ni values obtained by the subtraction of TAPPP deposition rate from deposition rates of NiTAPPP.

estimated by subtraction of the corresponding TAPPP deposition rate, is given in the last two columns of Table II. Occasional samples in the series were analyzed by atomic absorption spectroscopy, the results being given in the 2nd and 3rd columns of Table II. It is clear that the Ni content, estimated from deposition rates, is considerably higher than the Ni content determined by atomic absorption. This implies that the presence of Ni increases the TAPPP deposition rate due to interaction. A possible mechanism would involve reaction in the plasma phase or at the surface, with the heat of reaction dissipated to the substrate. This would generate a less volatile intermediate species, with a higher sticking coefficient, hence a higher deposition rate.

This hypothesis is supported by two observations made for evaporation of Ni metal into a flow of TAP monomer (no glow discharge). First, a significant drop in P_m is observed on initiation of metal flux. This indicates a sudden decrease in TAP concentration in the gas phase. Second, a brown–black film was deposited on the reactor walls as a result of the nickel evaporation into TAP vapor. Infrared spectra obtained for this film showed the same bands as reported for TAP monomer. Clearly, some interaction of the nickel and phosphine or allyl moiety occurs, since TAP is not deposited in the absence of the nickel evaporation without the aid of the glow discharge. The film proved to be volatile, disap-

pearing after several days in the open laboratory. A possible cause may be the oxidation of Ni metal, releasing TAP.

ESCA

ESCA spectra were obtained for three samples: (1) NiTAPPP, (2) a thin film of TAPPP exposed to Ni $(CO)_4$, and (3) a thin plasma polymer film made from nickel evaporated into an ethane glow discharge (NiEthPP). We have demonstrated that the second sample contained $Ni(CO)_x$, complexed to phosphine groups in TAPPP.[1] The first sample (NiTAPPP) was prepared in such a way that ESCA results could be compared with infrared spectra and atomic absorption results for juxtapositioned preparations. Table II indicates the relative positions of glass coverslips (columns 2 and 3) and Al foil strips

Table III   Ratio of Elements Obtained from ESCA of Plasma Polymer Thin Films

Sample	Relative Number of Atoms			
	Ni	P	O	C
NiTAPPP	1	3.7	17.0	33.9
TAPPP/Ni (CO)₄	1	2.9	8.4	31.1
NiEthPP	1	—	7.5	33.0

Table IV   ESCA Parameters for Plasma Polymer Films of Three Different Plasma Polymer Samples[a]

Element	Pos. (eV) for NiTAPPP	Width (eV) for NiTAPPP	Relative Amount for NiTAPPP[b]	Relative Amount for TAPPP/Ni (CO)$_4$[c]	Relative Amount for NiEthPP[d]	Assignment
C	284.6	2.1	4310	8730	5700	Hydrocarbon
	285.6	2.1	3950	3230	1720	$C-O$
	288.8	2.1	400	560	330[e]	$C=O$
O	530.0	2.3	980	990[f]	190[h]	$O-Ni$,
						$O-P$
	531.8	2.3	3150	2890[g]	1470[j]	$O-C$
	533.4	2.3	580	595	280	$O=C$
Ni	855.5	2.1	39	167[k]		$Ni-P$
	857.0	2.1	105	207[m]	162[n]	$Ni-O$
	857.8	2.1	104		40[p]	$Ni-O$
						$P-C$,
P	131.9	2.0	180	420[s]		$P-Ni$
	133.5	2.3	731	695[t]		$P-O$

[a] Deviations from indicated position, or width of curve-fitting peak of greater than 0.1 eV for TAPPP/Ni (CO)$_4$ and NiEthPP, are given in footnotes.
[b] TAPPP/Ni (CO)$_4$ is the sample prepared when a TAPPP is exposed to nickel tetracarbonyl.
[c] NiTAPPP is the sample of the codeposit of evaporated Ni and TAP plasma polymer.
[d] NiEthPP is the sample prepared using evaporated Ni and an ethane plasma polymer.
[e] Position = 288.5 eV, width = 2.0 eV.
[f] Position = 529.7 eV, width = 2.1 eV.
[g] Position = 531.6 eV.
[h] Width = 2.1 eV, assignment is $O-Ni$.
[j] Position = 532.1 eV.
[k] Width = 2.3 eV.
[m] Width = 2.9 eV.
[n] Position = 856.2 eV, width = 2.8 eV.
[p] Position = 857.6 eV, width = 3.0 eV.
[s] Position = 131.3 eV, width = 2.1 eV.
[t] Position = 133.0 eV, width = 2.1 eV.

(columns 4 and 5) at positions 1 and 2 of the reaction chamber. The mass %Ni in the NiTAPPP deposits, determined by atomic absorption spectroscopy, is shown for the glass coverslips. An ESCA spectrum was obtained from Al foil at a height of 2.75 cm from the reactor bottom, that is, in the position between the plasma polymers of 20.4 and 11.6% Ni by weight on the glass.

Elemental composition and relative functional group concentrations for the surface (50–100 Å depth) of the Ni-containing plasma polymer films was obtained from the analysis of the ESCA spectra. The relative amounts of the elements (Ni, C, O, and P) for the three preparations are given in Table III. It is seen that all three have approximately the same C/Ni ratio. For comparison with Table II, the mass % of Ni in the NiTAPPP sample in Table III is 6.4% (9.2% with the exclusion of oxygen). A C : H ratio of 1.65, as obtained for TAPPP, was assumed.[1] The mass % nickel obtained from the ESCA data is somewhat lower than that obtained by atomic absorption on neighboring glass blanks.

Curve fitting was used to divide the ESCA spec-

trum obtained for each element into component parts. The presence of phosphorus in the plasma polymer induces an additional component to the Ni $3p_{1/2}$ peak. The position of the additional component is consistent with the formation of a Ni–phosphine coordinate-covalent bond. This is particularly convincing for the TAPPP/Ni(CO)$_4$ system. The criteria used to select additional functional groups were: (1) presence of the groups is indicated either from general knowledge of the chemical system or from infrared spectra and (2) agreement is obtained between the relative amount of a functional group obtained by curve fitting to ESCA spectra for two distinct elements.

The relative amounts of functional groups derived from the ESCA spectra and the binding energy assignment for each component is as given in Table IV. The carbon signal for NiTAPPP can be reasonably fit using three curves, as shown in Figure 3(A). The parameters for this set of curves are given in Table IV. The curves and the assigned chemical environments of the oxygen, phosphorus, and nickel regions of the ESCA spectrum are shown in Figures
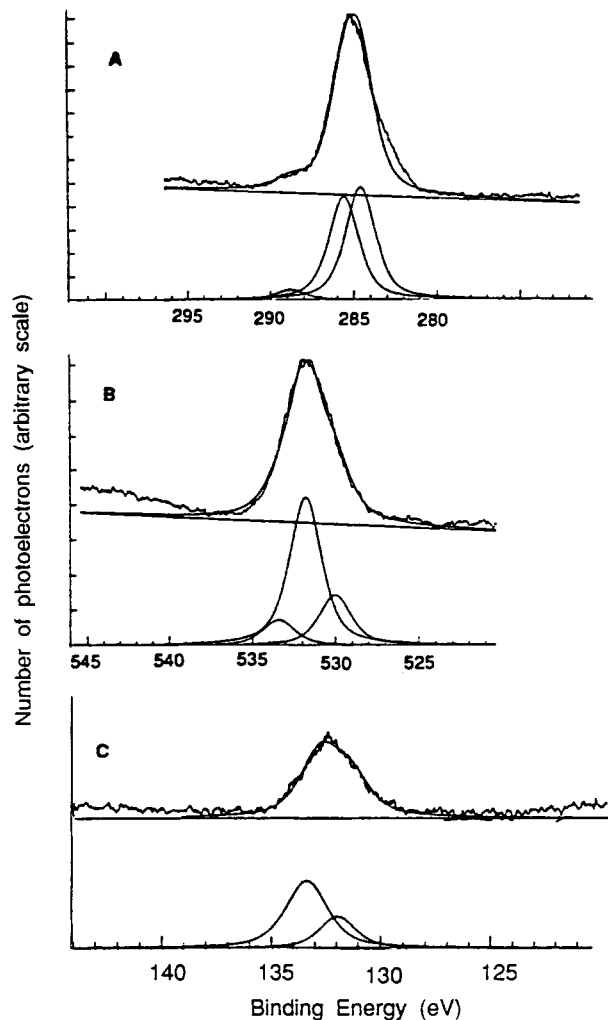
Figure 3 ESCA spectra for a NiTAPPP sample: (A) C 1s, (B) O 1s, (C) P 2p.

gives a very strong signal in these samples, due to the surface nature of the ESCA technique and the propensity for plasma polymers to react with O_2.[14] The peaks at 530 eV result from oxygen bound to nickel or phosphorus, while the peaks at 532 eV are from oxygen bonded to carbon or surface-adsorbed water.[15] The peaks around 533 eV indicate oxygen bound to carbon as in a ketone group.[16]

The P 2p peaks are easily resolved into two curves of 2.00 to 2.25 eV width at half height (Table IV). These curves represent P bound to the hydrocarbon backbone as phosphine and phosphine oxide, respectively.[17] The respective binding energies are 133 and 131.5 eV. This is illustrated in Figure 3(C) for NiTAPPP.

The Ni signals observed in the ESCA spectra can be fit by curves representing two or three distinct chemical environments, and are shown in Figure 4. The curve for Ni bound to phosphine ligands is observed at 855.5 eV, while the two other curves centered at 856.2 and 857 eV indicate Ni present as the oxide.[16,18]

The equivalence obtained for various functional groups from the curve fitting to peaks for various elements is shown in Table V. For example, the groups C—O and C=O are seen to exhibit the same relative population from curve fitting to both the C_{1s} and O_{1s} peaks, and the sum of O—Ni for Ni and O—P for P yields which was obtained for a single component of the O_{1s} peak.

Reaction of NiTAPPP with CO

An additional attempt to ascertain the environment of Ni atoms in the NiTAPPP film was made by reacting the film with CO gas. The infrared spectrum
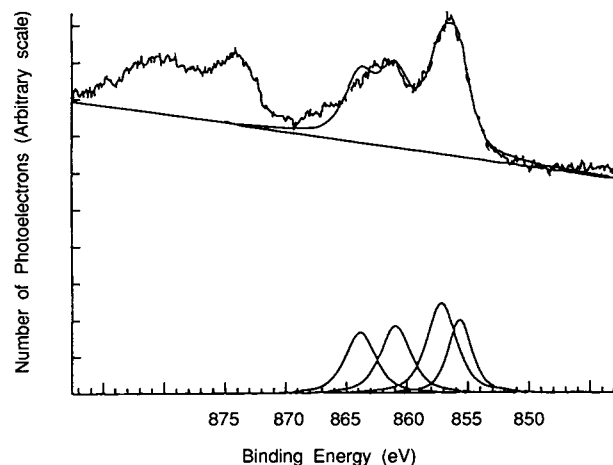
3(B), 3(C), and 4, respectively. The chemical assignments for the three fitted curves are also given in Table IV. The carbon 1s peak is conventionally resolved into four components at 284.6 eV (aliphatic, aromatic, or graphitic), 286 eV (C—O), 287.5 eV (C=O), and 288 eV (carboxylate group in an ester or carboxylate ion).[12,13] The three carbon signals observed for the plasma polymers indicate that a large quantity (45–65%) of the carbon present is in a nonoxygen bound form in the polymer backbone. The rest of the carbon has reacted with ambient oxygen. The peaks at 286 eV are indicative of hydroxyl groups attached to the carbon, while the peaks at 288 eV are derived from aldehydic or ketonic carbonyl groups or a carboxylate.

The O 1s signal is resolved into three curves (Table IV) and is illustrated for NiTAPPP in Figure 3(B). The environment is for oxygen bound to the elements found in the plasma polymer films. Oxygen

Figure 4 Curve fitting of Ni $2p_{3/2}$ ESCA spectrum for TAPPP with Ni(CO)$_4$.

Table V   Relative Population of Functional Groups Determined by ESCA

Functional Group	C_{1s}	O_{1s}	P	Ni
TAPPP/Ni (CO)$_4$				
C—H & P—C	8730			
C—O	3230	2890		
C=O	560	595		
O—Ni				207
O—P		(990)	695	
Ni—P			(420)	167
P—C				
NiTAPPP				
C—H & P—C	4310			
C—O	3950	3150		
C=O	400	580		
O—Ni				209
O—P		(980)	695	
Ni—P			(180)	39
P—C				
NiEthPP				
C—H	5700			
C—O	1720	1470		
C=O	330	280		
O=Ni		190		202

of metal carbonyl adducts yields information regarding the presence of other ligands attached to the metal. Weight gain data were also obtained.

It was found that the relative nickel content of the NiTAPPP film had a dramatic effect on the mass of the film after exposure to CO gas. The effect of exposure to CO gas and subsequent evacuation is shown in Figure 5(A) for a film with *high* Ni loading. A net mass decrease is observed. Thin films of NiTAPPP exhibit stable mass when left in vacuum (24 h), but the mass of the NiTAPPP film changes when 160 torr of CO is bled into the reactor. An instantaneous mass gain of 0.8 μg cm^{-2} was recorded. When CO was removed and the vacuum was reestablished, the mass of the film decreased. Two stages are observed in the mass decrease. The mass drops almost immediately as the CO is removed, and then a slower decrease is observed until a constant value is obtained.

By contrast, a net mass increase is observed, after exposure to CO and subsequent evacuation, for a lightly nickel loaded NiTAPPP film. A typical gravimetric trace is shown in Figure 5(B) for this case.

The source of mass loss for the heavily loaded film is assumed to be the formation of volatile Ni(CO)$_4$. This is reasonable since no mass loss was observed with similar experiments carried out with TAPPP. For lightly loaded NiTAPPP, volatilization of much of the Ni is prevented because of the coordination of individual Ni atoms to phosphine groups in the plasma polymer as well as to CO.

The loss of mass can be used to estimate the amount of Ni in the sample. If one assumes that phosphine bound nickel will not form volatile Ni(CO)$_4$, and that the composition of NiTAPPP
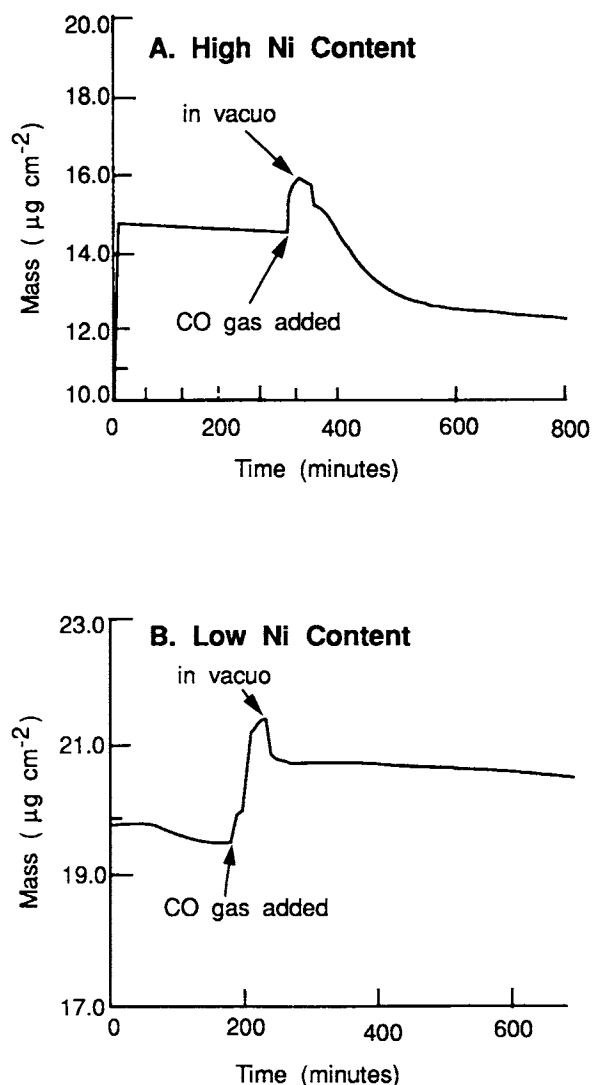

Figure 5   Mass of NiTAPPP codeposit exposed to 160 torr CO for 40 min with subsequent evacuation. (A) High nickel loading with deposition rates (μg cm^{-2} min^{-1}) as follows. Ni: 2.84; TAPPP: 1.37; NiTAP: 2.78. (B) Low nickel loading with deposition rates (μg cm^{-2} min^{-1}) as follows. Ni: 0.83; TAPPP: 1.03; NiTAP: 2.93.

with Ni bound to P is as given by the ESCA results, that is, $Ni_{1.0}P_{3.7}C_{33.9}H_{56.5}$, then the formula for the preparation including metallic Ni is $Ni_{3.0}P_{3.7}$-$C_{33.9}H_{56.5}$. This is to say that there are an additional two moles of metallic nickel per molecular formula. The hydrogen content in this formula was derived from the H/C ratio, as obtained by elemental analysis.[1]

Infrared spectra obtained for NiTAPPP, after exposure to CO and subsequent evacuation, confirm this interpretation. Three new IR absorption bands in the spectrum are observed when the NiTAPPP film is exposed to CO. These bands occur at 2048, 1988, and 1932 cm^{-1} (Fig. 6) and are all in the CO region that suggests linear coordination.[19] No bands for bridging carbonyl are observed. Earlier IR experiments using TAPPP without nickel did not give any evidence that CO reacts at the surface of the film; that is, there were no new IR bands in the carbonyl region 2300–1700 cm^{-1}.[1]

NiTAPPP Reaction with NO

While the data presented above for reaction of NiTAPPP with CO establish the presence of Ni bound to functional groups in the plasma matrix *after* the reaction, the origin of such complexed Ni is ambiguous. The gravimetric data suggest that $Ni(CO)_4$ is formed, and the reaction of $Ni(CO)_4$ with TAPPP has been shown[1] to yield a product with an IR signature similar to that of NiTAPPP reacted with CO. Thus, at least part of the ligand complexed Ni may have been formed by reaction of NiTAPPP phosphine groups with $Ni(CO)_4$ produced *in situ*.

To demonstrate by infrared spectroscopy that Ni bound to functional groups on the plasma polymer existed in NiTAPPP, *as formed,* it was necessary to carry out a reaction that did not result in the formation of a volatile product. In an effort to produce such a reaction, the polymer was reacted with NO gas.

NO was reacted with NiTAPPP at a pressure of 160 torr for 40 min. Film weight was plotted as a function of time (Fig. 7) for the NiTAPPP film before, during, and after the reaction with NO. An irreversible weight gain of 33.4% was observed after the system was degassed. The NiTAPPP preparation, which was reacted with NO, and was described above, corresponds to the lightly Ni loaded preparation used for reaction with CO. Since mass gain data were obtained at a different position in the reactor than was used for deposition of ESCA samples, the nickel content of the preparation on the depo-

sition rate monitor is expected to be higher than that indicated by the ESCA results. This assumption is confirmed by the high mass gain in NO. If one assumes that 1, 2, or 3 molecules of NO may react with each Ni atom, a formula, consistent with the observed weight gain, and in which the number of Ni atoms is less than that of P atoms, is possible only if 3 NO are bonded to each Ni. Alternatively, the weight gain may be explained by the reaction of each Ni with 2 NO and the oxidation of each P to PO, again requiring fewer than 1 Ni per each P. In fact, this calculation would have Ni bound to 90% of the phosphine groups, which contrasts with the ESCA results (for a sample formed at a different location), from which it was concluded that only 10% of the phosphine groups bound Ni. The assumptions made for NO and CO reacted with TAPPP are that the NO weight gain provides information regarding Ni bound to phosphine, whereas the weight loss for CO reacted with TAPPP (heavy Ni loading) provides information regarding the uncomplexed Ni.

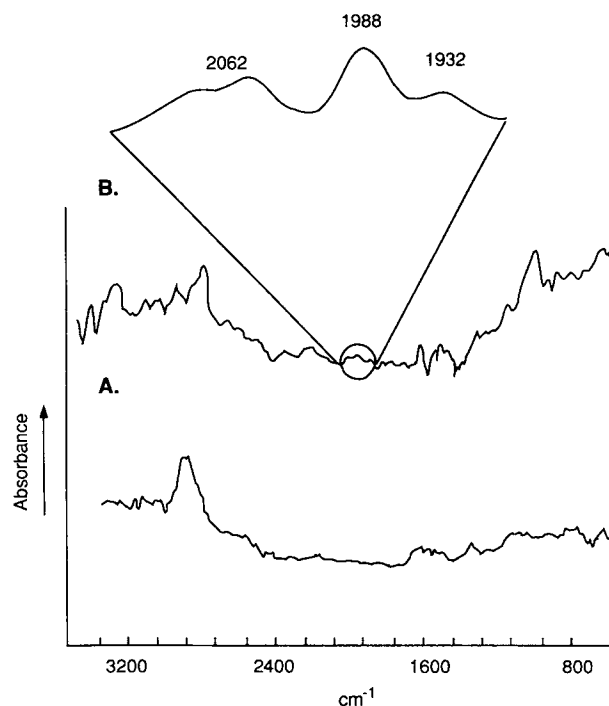The IR spectrum for NiTAPPP samples exposed to NO is similar to that obtained for samples of

Figure 6 IR-ATR absorption spectra of (A) NiTAPPP film coated on aluminum foil and (B) separately prepared NiTAPPP film coated on aluminum foil after exposure to CO at 160 torr for 40 min duration. Separate preparations were required because transfer to the FTIR spectrometer necessitated exposure to air.

TAPPP exposed to NO with the addition of two new bands at 1733 cm^{-1} and 917 cm^{-1}. A typical IR absorption spectrum of NiTAPPP exposed to NO is shown in Figure 8. The band at 1733 cm^{-1} is assigned to NO$^+$, coordinated to phosphine complexed nickel. This is a reasonable assignment, based upon the ν_{NO} of nickel nitrosyl complexes with the bidentate diphenylphosphinoethane ligand[19] and of a series of nickel nitrosyl complexes with substituted phosphine ligands.[20] The band at 917 cm^{-1} has not been assigned.

Adhesion

NiTAPPP films demonstrated poor adhesion to Al foil, being almost completely removed by Scotch tape. This is in contrast to TAPPP films, formed on aluminum foil substrates.[1]

DISCUSSION

The data presented above can be used to assemble a composite picture of NiTAPPP. The plasma polymer contains reactive phosphine groups, as shown previously in a study of TAPPP[1] and as may be inferred from the infrared spectrum of NiTAPPP before and after exposure to O_2. After such exposure, a band at 1160 cm^{-1} is seen to increase in intensity, signifying the oxidation of phosphine groups to phosphine oxide. The increase in the deposition rate on the walls of the reactor, beyond that expected from the sum of Ni deposition (as measured in a corresponding pressure of Ar), and TAPPP deposition, independently, may indicate the presence of specific interactions between phosphine groups and Ni atoms in the plasma phase. A more persuasive indicator that these interactions occur is the observation that Ni metal evaporated into flowing TAP
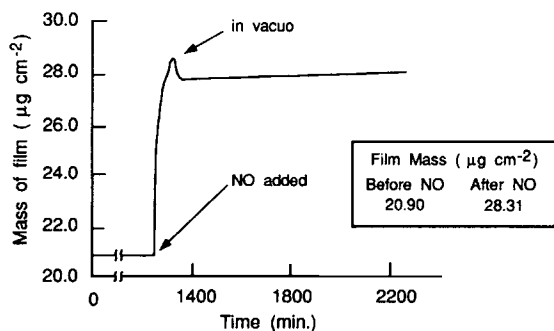

Film Mass (μg cm^{-2})	
Before NO	After NO
20.90	28.31

Figure 7 Plot of the mass of a NiTAPPP film as a function of time, exposed to 160 torr NO for 40 min and subsequently evacuated.

(no plasma) results in a markedly decreased P_m and deposition of an involatile layer on the reactor walls.

The fact that NiTAPPP contains Ni bound to phosphine groups is conclusively shown by the gravimetric and IR evidence obtained regarding the nature of the reaction of NO with the deposit. The NiTAPPP exposure to NO results in additional IR absorption bands at 1733 and 917 cm^{-1}, which indicate that a nickel nitrosyl complex has been formed. The absorption band at 1733 cm^{-1} falls into the NO frequency range observed for a series of nickel phosphine complexes with a bound nitrosyl cation.[19,20] The gravimetric data are consistent with near complete oxidation of phosphine groups and near complete binding of phosphine groups to Ni atoms, each of which reacts with two NO molecules. The reaction of NO with TAPPP has been studied before[1] and is consistent with this picture.

The interaction of CO with NiTAPPP is consistent with this picture, although not sufficient to prove it. New IR bands (Fig. 6) are observed when CO is reacted with NiTAPPP films. These absorption bands at 2062, 1988, and 1932 cm^{-1} correspond to those bands expected if a nickel carbonyl complex was formed.[21] It can be demonstrated that this is not a result of Ni metal reacting with CO. The IR bands observed for CO adsorbed on nickel metal are at 2080 cm^{-1} and 1940 cm^{-1}.[22] These bands were not interrelated in a consistent fashion and they are believed to arise from different species. Supported Ni on silica gave rise to three IR absorption bands at 2073, 1924, and 1870 cm^{-1} at high CO concentrations. At low CO concentrations, the intensity of the bands changed and the 2073 band shifted to 2040 cm^{-1}. This system of Ni supported in silica with low CO concentration is the closest solid phase analogy we have been able to find to the supported NiTAPPP film with IR absorption bands at 2062, 1988, and 1932 cm^{-1}. The significant shifts between Ni/silica (1924, 1870) and the lower wave-number bands observed for NiTAPPP (1988 and 1932), however, suggest an alternative explanation, that is, the formation of substituted nickelcarbonyl species. Normal mode analysis of monosubstituted Ni(CO)$_3$X and disubstituted Ni(CO)$_2$X$_2$ species indicates that two carbonyl IR bands should be observed for each species. These two bands are observed for a plethora of substituted nickelcarbonylphosphine complexes. For monosubstituted complexes, ν_{CO} has two ranges, 2080-2040 cm^{-1} and 2000-1975.[23] The two ν_{CO} ranges for disubstituted complexes are 2020-1990 and 1950-1920 cm^{-1}.[23] It follows that a mixed population of mono- and disubstituted nickelcarbonyl complexes would yield a spectrum such as the spectra
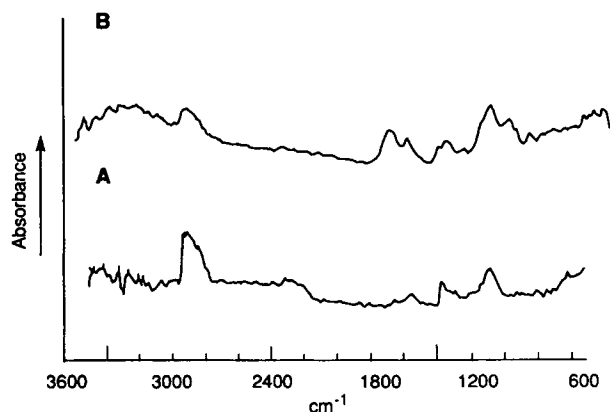
Figure 8 IR-ATR absorption spectra of (A) TAPPP and (B) NiTAPPP, exposed to 160 torr NO for 40 min and subsequently evacuated.

obtained for NiTAPPP exposed to CO. Furthermore, the band at 1988 cm^{-1} is more intense than either of its neighbors, consistent with it being the sum of two peaks, each of intensity equal to that of 2062 and 1932 cm^{-1}. It should be noted that a similar infrared signature was obtained for TAPPP reacted with Ni(CO)$_4$; that is, the absorption bands are at 2048, 1988, and 1930 cm^{-1}.[1] However, the band at 1930 cm^{-1} is considerably stronger for the TAPPP + Ni(CO)$_4$ sample than it is for NiTAPPP. This implies that a considerably greater fraction of phosphine bound Ni is dicoordinated to the phosphorus in the Ni(CO)$_4$ + TAPPP sample, relative to the NiTAPPP sample.

The Ni atoms trapped in coordination sites in NiTAPPP are likely to be coordinatively unsaturated. Their consequent high reactivity may explain why the ESCA spectra, obtained after exposure of the samples to air, makes a less convincing case for the presence of residual Ni-P bonds on the surface of the NiTAPPP sample than for the TAPPP + Ni(CO)$_4$ sample.

A majority of the nickel atoms are oxidized after exposure to air, even for the TAPPP + Ni(CO)$_4$ sample, where all Ni atoms must have originated by coordination to phosphine groups. Thus, the phosphine region of an ESCA spectrum displays chemical environments corresponding to the oxidized phosphine, which is phosphine oxide and carbon or nickel bound phosphine (see Table IV). The ESCA evidence for these two phosphorus chemical environments is twofold. First, the phosphorus band is fit by two curves with reasonable chemical shifts for these assignments. Second, a rough correlation between the equivalents of different elements in the same chemical environment indicate a bonding

stoichiometry. For example, the phosphine oxide signal from TAPPP exposed to Ni(CO)$_4$ has approximately 700 units in relative amounts in both the oxygen and phosphorus regions of the spectrum (see Table V). This corresponds to the 1 : 1 stoichiometry expected for P=O. The second phosphine signal, with a relative intensity of 420 units, is in excess of the approximately 170 units of nickel bound to phosphine. This confirms the IR indicated preponderance of nickel bound by two phosphines since the ratio is approximately 2 : 1.

The fact that (O—Ni + O—P) is in rough correspondence for the P and Ni spectra on the one hand, and the O$_{1s}$ on the other, confirms that the 167 units assigned to Ni—P are reasonable, not only on the basis of the position of that component, but because it is consistent with assignments made for other elemental spectra as well. Although there is a component in the P$_{2p}$ spectrum consistent with a P—C (phosphine group), the expected signal for carbonyl in the C$_{1s}$ and O$_{1s}$ regions is calculated as being too small, relative to other functional groups, to make a perceptible contribution.

Arguments such as those above are not as readily made for the Ni—P contribution to the NiTAPPP spectrum (see Table V) because of its relatively small contribution. It is thus observed that Ni-TAPPP, *after exposure to air,* has little or no phosphine bound Ni. This is consistent with the presence of coordinatively unsaturated, and therefore highly reactive, Ni atoms in this sample.

Not all Ni in the NiTAPPP film, as formed, is bound to phosphine groups. The presence of elemental nickel, which becomes preponderant at high ratios of Ni evaporation rate to NiTAPPP deposition rate, has been suggested by the loss of weight for samples with high nickel loading upon exposure to CO. Undoubtedly some free nickel is present in the low nickel loading samples as well. The possibility that nickel is bound to allyl groups in the plasma polymer exists, although no direct evidence is observed for this in the IR spectrum ($\nu_{c=c}$ remains unchanged).

Both elemental Ni and phosphine bound Ni are oxidized. The latter is expected from the known air sensitivity of metal phosphine complexes. The presence of oxidized Ni is indicated by two contributions to the Ni$_{3P_{1/2}}$ spectrum corresponding to NiO and Ni(OH)$_2$.

CONCLUSIONS

A crosslinked plasma polymer containing phosphine groups complexed to Ni atoms is formed when Ni

metal is evaporated into a TAP glow discharge. Such a plasma polymer contains both coordinated and uncoordinated Ni; the relative proportions of these moieties depends on the (Ni evaporation rate)/ (TAPPP plasma polymer deposition rate) ratio. NiTAPPP contains reactive, coordinatively unsaturated Ni phosphine centers, which are readily available for reaction with small molecules. The film is insoluble in solvents for TAP and metal phosphines. The preparation method described in this article represents a general method for the production of crosslinked polymeric thin films that contain coordinated transition metals. This statement is based on the fact that the plasma polymerization technique can be applied to any volatile reactant and that any metal can be evaporated using either resistive heating, as in this work, or e-beam techniques.

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