

Adsorption of a Silver Chemical Vapor Deposition Precursor on Polyurethane and Reduction of the Adsorbate to Silver Using Formaldehyde

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The interaction of the silver chemical vapor deposition precursor (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)(trimethylphosphine)silver(I), [(fod)AgP(CH₃)₃], with a polyurethane surface has been investigated with reflection–absorption infrared spectroscopy (RAIRS), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). The RAIR spectra show a decrease of the intensity of both polyurethane C=O and N–H vibrational bands at 90, 300, and 340 K. This suggests that a specific interaction occurs between [(fod)Ag(PMe₃)] and polyurethane carbonyl groups at the surface, leading to the displacement of [P(CH₃)₃]. After exposure of polyurethane to the Ag complex at room temperature and above, XPS shows the presence only of Ag, F, and O, indicating displacement of [P(CH₃)₃] groups. The exposure of the adsorbed (fod)Ag–polyurethane complex to formaldehyde [HCHO] leads to additional deposition of silver and to the formation and the desorption of [1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione], [fodH], from the polyurethane surface. AFM indicates that the silver is present in the form of clusters. Taken together, these data demonstrate the feasibility of low-temperature CVD of silver on organic polymer substrates.

Introduction

Polymer surface chemistry is a growing field with many industrial applications in advanced composite materials, where coatings can modify wettability, adhesion, friction, and biocompatibility,¹ but the low surface energy and reactivity of polymers creates problems in the production of metal coatings. Polymer surfaces can however be modified to enhance their physical or chemical properties without affecting the bulk properties of the polymer. For example, the surface energy of polymers can be increased by ion bombardment² and plasma treatment³ in order to incorporate chemical groups or to create radicals on the surface that can then act as nucleation sites for desired reactions. For metal coatings applications, physical vapor deposition (PVD) is a well-established technique, but apart from the possibility of surface damage,⁴ PVD methods cannot be used to coat complicated shapes if there is not line-of-sight from the source to the substrate. Metal–organic chemical vapor deposition (MOCVD) is a growing field of research for metal thin-film deposition, particularly for selective and conformal deposition. The possibility of conformal coating is one of the major motivations for attempting to deposit metals on polymers from organometallic sources. A major general difficulty with this approach is that the removal of the ligands must be accomplished at a temperature below the decomposition temperature of the polymer.

In this article, we report results of a study on the adsorption and reaction of a silver complex [(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)(trimethylphosphine)silver(I)], [(fod)Ag(PMe₃)],⁵ on the surface of polyurethane (PU). Since silver has antibacterial properties, silver coating of polyurethane catheters would have useful biomedical applications. The precursor has shown the best thermal stability during the process of volatilization and the lowest temperature for silver deposition (below room temperature) on Ag(111) and Pt(111) single

crystals.⁶ Similar behavior has been observed with [(1,1,1,2,2,3,3-heptafluoro-7,7-diethyl-4,6-octanedionato)(triethylphosphine)silver(I)], [(fod)Ag(PEt₃)].^{7,8} These fod complexes have not been structurally characterized, but all spectroscopic data indicate that they contain 3-coordinate silver(I) as proved crystallographically for the closely related complex [CF₃-COCHCOCF₃)Ag(PEt₃)].⁵ We demonstrate that deposition of Ag in the form of clusters is possible at 300–340 K and that the deposition can be enhanced by exposure of the complex adsorbed on the polyurethane surface to gas-phase HCHO.

We recognize the importance of strong adhesion in applications of metal films on polymers, but in this report we concentrate upon the chemistry of the interaction of the precursors with PU; we will report elsewhere upon efforts to modify the PU surface to enhance adhesion.

Experimental Section

The experiments were performed in two separate UHV chambers. Reflection–absorption infrared measurements were performed in the UHV chamber (base pressure $<5 \times 10^{-9}$ Torr, mainly water) described previously,^{7,8} the only difference being that the coldfinger is terminated with a sample holder that can accommodate interchangeable aluminum disks of 14 mm diameter. A wobble stick was used to interchange samples that were held on a carousel. A heater cartridge (7.6 mm diameter and 10.2 mm long) was located at the back of the sample holder to allow sample heating, and a chromel–alumel thermocouple was set between the sample and the heater cartridge to monitor the sample temperature from 90 to 600 K. This chamber is equipped with a mass spectrometer (Hiden-601), an ion gun (Varian-2046), and a quartz crystal monitor (Leybold Inficon) as well as a microwave source for remote plasma treatment of the polymer films. A Mattson Cygnus-100 spectrometer was employed for RAIRS measurements that were made in grazing (7°) incidence geometry. A liquid nitrogen cooled, narrow-

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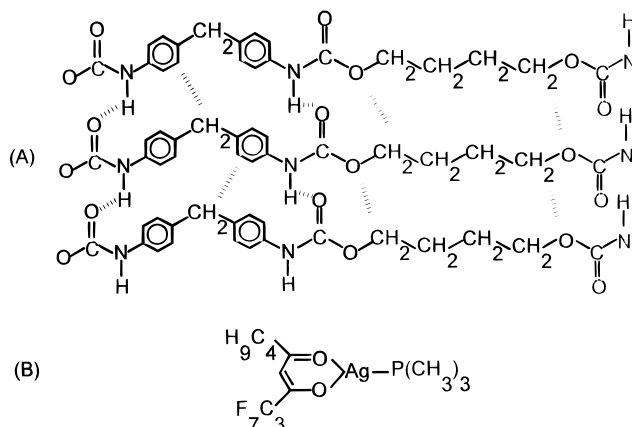
band mercury–cadmium–telluride (MCT) detector was used to collect the RAIRS data. Typical data acquisition involved co-adding 500 scans at a resolution of 4 cm^{-1} . All RAIR spectra are presented without background correction.

The X-ray photoelectron spectroscopy (XPS) measurements were performed in a chamber described elsewhere⁹ using an SSL SSX-100 X-ray photoelectron spectrometer with a monochromatized Al K α X-ray source and hemispherical analyzer. Elemental analysis was performed using a spot size of $600\text{ }\mu\text{m}$ and a pass energy of 129 eV, whereas for the high-resolution measurements they were set to $300\text{ }\mu\text{m}$ and 54 eV, respectively. XPS analyses were performed at a takeoff angle of 53° . An electron flood gun was used to compensate for charging effects (1 V, 0.05 μA). The binding energies (BE) shown were calibrated against a C 1s BE of 285.0 eV for the CH_2 carbons in the polymer.¹⁰ The spectra were deconvoluted after subtraction of a Shirley background using Gaussian–Lorentzian product function of width 1.0–1.2 eV. The components were in all cases consistent with chemical evidence.

The atomic force microscopy measurements were carried out with a Digital Instruments MultiMode SPM¹¹ Nanoscope IIIa controller operated in the standard tapping mode.¹² In tapping mode, the cantilever on which the probe tip is mounted is excited into resonance with a piezoelectric driver. Typically the tip–cantilever was oscillated at high frequency ($\sim 300\text{ kHz}$) with a fairly high amplitude ($\sim 10\text{--}300\text{ nm}$), so that the tip tapped the surface once during each period. The oscillation amplitude is used as a feedback signal to measure topographic variations of the sample. To assist in removing topographic contrast, we also made use of phase mode imaging. In phase mode imaging the phase lag of the cantilever oscillation relative to the signal sent to the cantilever piezodriver is recorded by the Nanoscope IIIa controller using an extended electronic module. The phase lag is sensitive to spatial variations in composition, viscoelasticity, and adhesion.^{11,13} This makes phase mode imaging useful for high-resolution mapping of these properties. The resolution is often comparable to the full resolution in tapping mode imaging. The use of the extended electronic module enables recording of changes of the phase lag and the amplitude variation of the cantilever oscillation while recording the tapping mode topography. These signals are displayed simultaneously in real time, giving up to three complementary images of the same area, which simplifies the image analysis considerably. Amplitude mode imaging often has lower spatial resolution but otherwise gives similar information as phase mode imaging. All imaging was done with filters off. The standard “J” scanner head was used, which has a maximum scan range of $\sim 150\text{ }\mu\text{m}$. The interleaved scan rate was 0.5–3 Hz. Measurements were performed in laboratory air at room temperature. Nanoprobe tips¹⁴ were used with resonance frequencies $\sim 250\text{--}340\text{ kHz}$ and force constants $\sim 18\text{--}46\text{ N/m}$. The raw data of the AFM images were fitted to an 0–3 order plane by the Nanoscope IIIa 4.22 software and imported to the shareware program NIH Image 1.60,¹⁵ where the contrast was enhanced further. The root-mean-square (rms) roughness and the maximum height variation in topography (compared to a perfect plane) of the plane-fitted unfiltered images were calculated using Nanoscope IIIa software.

A new UHV compatible doser was built to minimize dissociation of low vapor pressure precursors during the process of volatilization. Details of the construction of this doser are given elsewhere.¹⁶ This differentially pumped doser sets the precursor reservoir within 2 cm of the sample and can be loaded and unloaded without breaking vacuum. The exposures quoted

SCHEME 1: (A) Molecular Structure of Aromatic Polyurethane and Possible Hydrogen Bond between Polymer Chains; (B) Molecular Structure of [(fod)Ag(PMe₃)] Precursor



in the figures are in langmuirs from the ion gauge pressure readings (1 langmuir = $1 \times 10^{-6}\text{ Torr}\cdot\text{s}$). The actual exposures at the sample will be much higher because of the directional nature of the dosing. Also, the ion gauge sensitivities for these molecules relative to nitrogen are unknown but are $\gg 1$. The exposures are therefore intended as a relative guide only.

Polyurethane films were prepared by spin casting from THF solution (1% w/w) at 2000 rpm onto polished Al disks. The polyurethane used in this study is a medical grade aromatic polymer (Tecothane trade mark) used to make catheters and was obtained from Thermedics. The molecular structure of this polymer is shown in Scheme 1. The molecular weights of this polymer are $M_n = 15\,000\text{--}30\,000$ and $M_w = 250\,000\text{--}300\,000\text{ g mol}^{-1}$. Prior to each experiment these films were placed under vacuum for several hours to remove adsorbed water. Paraformaldehyde (95% purity) and formic acid (88% purity) were obtained from Aldrich. Formaldehyde was obtained by pyrolysis of paraformaldehyde at 400 K. The formic acid was degassed by repetitive freeze–pump–thaw cycles.

Results and Discussion

A. Reaction of [(fod)Ag(PMe₃)] and Polyurethane. *RAIRS Results of the Adsorption of [(fod)Ag(PMe₃)] on Polyurethane.* We first present RAIRS data for the adsorption of the [(fod)-Ag(PMe₃)] on the polyurethane surface maintained at different temperatures (Figure 1). The data for the precursor-exposed polyurethane surfaces are displayed as difference spectra using the RAIRS spectrum of the polyurethane surface as the background. A decrease (negative-going peak) in the intensity of a band for the polymer, for example, indicates either removal or reaction of the functional group by interaction with the OM precursor, although we must also consider physical effects such as those described by Strunkus et al. These authors report¹⁷ that metal clusters can perturb the electric dipole of a given normal mode or group frequency of a polymer surface functional group without a strong *chemical* interaction. In light of the reactivity of the surfaces demonstrated in this paper, we propose that in the present circumstances a chemical interaction does occur. Figure 1 illustrates IR spectra of the precursor in a KBr disk (A), the polyurethane film (B), and the difference spectra (the background is polyurethane/Al) obtained after exposure of the film to the precursor at 90 K (C), 300 K (D), and 340 K (E). The difference spectra (C, D, E) all show that the carbonyl vibrational bands at 1734 and 1705 cm^{-1} decrease upon

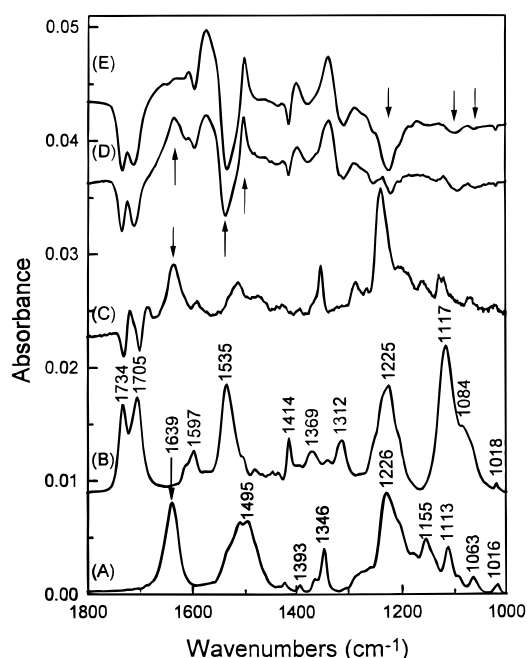


Figure 1. (A) FT-IR transmission spectrum of [(fod)Ag(PMe₃)] in KBr and (B) RAIR spectra of a polyurethane film on Al disk. RAIR spectra acquired after the adsorption of [(fod)Ag(PMe₃)] on polyurethane at (C) 90 K (7.2×10^4 langmuirs); (D) 300 K (1×10^6 langmuirs); (E) 340 K (7.2×10^5 langmuirs). Spectra C–E are difference spectra utilizing the spectrum of the untreated PU surface as the background.

TABLE 1: Observed Vibrational Frequencies and Band Assignments for [(fod)Ag(PMe₃)]^a

band assignt	[(fod)Ag(PMe ₃)] in KBr	[(fod)Ag(PMe ₃)] on polyurethane at 90 K
$\nu_a(\text{CH}_3)$	2970 s	2975 w
$\nu_a(\text{CH}_2)$	2930 m	2945 w
$\nu_s(\text{CH}_3)$	2907 m	2922 w
$\nu_s(\text{CH}_2)$	2872 m	2883 w
$\nu(\text{C=O})$	1639 vs	1634 vs
$\nu(\text{C=C})$	1510 vs	1514 m
$\delta(\text{CH}_3)$	1495 vs	1508 m, 1471 m
$\nu(\text{CC}) + \delta(\text{CH}_2)$	nr	1427 m
$\nu(\text{CCF}_3)$	1393 vw	1391 vw
$\delta(\text{CH}_3)$	1346 s, 1316 vw	1350 s, 1300 w
$\nu_a(\text{CF}_2)$	1267 m	1282 m
$\nu_a(\text{CF}_3)$	1226 vs	1235 vs
$\nu_s(\text{CF}_3)$	1177 m	1195 m
$\nu(\text{C-C}) + \delta(\text{CH})$	1155 m, 1113 m	1165 m, 1121 m
$\rho(\text{CH}_3)$	1016 w, 960 w	1069 w, 969 w

^a All frequencies are given in cm^{-1} . The assignments of these bands are based on reported data of species containing such groups.²⁶ nr, not resolved; v, very; s, strong; m, medium; w, weak.

exposure at all three temperatures, indicating that both free (1734 cm^{-1}) and hydrogen-bonded (1705 cm^{-1}) carbonyl groups present at the polyurethane surface react readily with the precursor. Figure 1C shows that the intact Ag precursor condenses at 90 K, since the spectrum obtained at this temperature is similar to the KBr disk transmission spectrum of [(fod)Ag(PMe₃)] (Figure 1A). The attribution of vibrational bands of the precursor and polyurethane is given in Tables 1 and 2, respectively.^{18,19}

Adsorption of [(fod)Ag(PMe₃)] at 300 and 340 K led to the formation of additional negative peaks at 1535 and 1225 cm^{-1} (hidden at 90 K by vibrational bands of the Ag complex) and, only in the case of adsorption at 300 K, a positive peak at 1639 cm^{-1} . The two negative peaks correspond to the $\delta(\text{N-H})$ deformation of polyurethane, whereas the positive peak corre-

TABLE 2: Observed Vibrational Frequencies and Band Assignments for Polyurethane Film on Al Disk^a

band assignt	polyurethane on Al	band assignt	polyurethane on Al
$\nu(\text{N-H})$ bonded	3325 m	$\nu(\text{C-H})$ methylene	2943 s
N-H			
$\nu(\text{N-H})$ cis-trans isom	3186 vw	$\nu(\text{C-H})$ methylene	2935 s
$\delta(\text{N-H}) + \nu(\text{C-N})$	1535 vs	$\nu(\text{C-H})$ methylene	2859 s
$\delta(\text{NH}) + \nu(\text{CN}) + \beta(\text{CH})$	1312 s	$\nu(\text{C-H})$ methylene	2797 m
$\delta(\text{N-H}) + \nu(\text{C-N})$	1225 vs	$\omega(\text{C-H})$ methylene	1369 w
$\nu(\text{C=O})$ urethane	1705 vs	$\delta(\text{C-H})$	1117 vs
$\nu(\text{C-O})$ urethane	1225 vs	$\rho(\text{CH}_2)$ methylene	774 w
$\nu(\text{C-O})$ urethane	1075 s	$\nu(\text{C-H})$ aromatic	3067 vw
$\nu(\text{C=O})$ ester	1734 vs	$\nu(\text{C=C})$ aromatic	1597 m
$\nu(\text{C-O})$ ester	1175 nr	$\nu(\text{C-C})$ aromatic	1414 m
$\nu(\text{C-O})$ ester	1065 s	CH out-of-plane aromatic	818 w

^a All frequencies are given in cm^{-1} . Band assignments are based on reported data.¹⁹ v, very; s, strong; m, medium; w, weak; β , in-plane binding; ω , wagging; ρ , rocking; nr, not resolved.

sponds to the $\nu(\text{C=O})$ vibrational band of the adsorbed precursor. This result suggests that the N-H groups are also involved in the reaction between the incoming Ag complex and polyurethane. The asymmetric shape of the vibrational band near 1535 cm^{-1} is due to the combination of the increase of the $\delta(\text{CH}_3)$ mode intensity due to the presence of adsorbed Ag complex and to the decrease of the $\delta(\text{N-H})$ intensity for the polymer due to the interaction of these groups with the precursor. The RAIR spectra (Figure 1D,E) show also a small decrease of the vibrational peaks at 1075 and 1065 cm^{-1} , which indicates that ester functional groups (C-O) present on the surface are participating in the reaction during the adsorption of the Ag complex. The very low intensity of these vibrational bands is probably due to their orientation along the polymer chains. This could place them parallel to the plane of the Al-mirror surface in our spin-coated samples, rendering them less detectable because of the operation of the so-called “surface selection rules” of the RAIRS technique. These selection rules indicate that, in the reflection geometry, only modes possessing dipole active components perpendicular to the metallic surface are detected. More evidence on the participation of these functional groups was obtained from C 1s, O 1s, and N 1s XPS data (see below).

The RAIR spectrum of the adsorption of the [(fod)Ag(PMe₃)] on polyurethane films at 340 K shows higher intensity of vibrational bands compared to the RAIR spectrum obtained at 300 K. This increase in the intensity is due to the change in surface reactivity which could arise simply from thermal activation of the precursor or to changes of the mobility of polyurethane chains (diffusion of low molecular weight polymer chains from the bulk to the surface) and/or to the change of the orientation of carbonyl and N-H groups, each of these making more active sites available for the adsorption of the silver complex. The absence of a C=O vibrational band at 1639 cm^{-1} in the spectrum at 340 K is probably due to partial dissociation of the (fod)-Ag bond or to the orientation of the [fod] ligand with its carbonyl groups parallel to the surface. Studies of the adsorption of [fodH] and [(fod)Ag(PMe₃)] on metal surfaces have shown that the first adsorbed states of these molecules are characterized by having their molecular plane parallel to the surface.⁶⁻⁸

XPS Results of the Adsorption of [(fod)Ag(PMe₃)] on Polyurethane. It was not possible to carry out XPS measurements at 90 K, but wide scans of the exposed surface at room temperature (not illustrated) indicated the presence of Ag and F as well as N, C, and O, but the complete absence of the P 2p

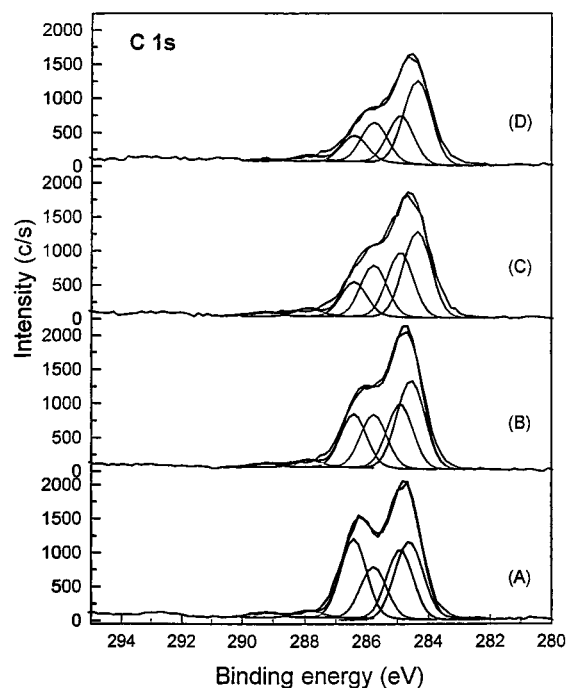


Figure 2. C 1s spectra of variously treated polyurethane spin-cast films: (A) polyurethane film on Al disk, (B) [(fod)Ag(PMe₃)]/polyurethane (1.8×10^5 langmuirs), (C) [(fod)Ag(PMe₃)]/polyurethane (2.8×10^5 langmuirs), (D) [(fod)Ag(PMe₃)]/polyurethane (3.9×10^4 langmuirs), exposed to HCHO. All exposures made at 300 K.

peak near 200 eV, providing direct evidence that the [PMe₃] group is displaced on chemisorption. In addition, the F:Ag ratio on the exposed surface is 0.6:1 compared to 7:1 for the intact complex, indicating substantial dissociation of fod–Ag bonds and desorption of [fod] ligand. The binding energy (683.9 eV) of a part of fluorinated species remaining on the surface corresponds to species in the form of [C_xF_y] or [C_x(O)F_y] on metal substrates. From these data we must conclude that the precursor is dissociated on the surface at room temperature. XPS data and AFM images presented below indicate that at least some of the silver (probably most) is reduced to the metallic form and exists on the surface in small Ag clusters.

Figure 2 shows narrow scan C 1s spectra of the polyurethane film (A) and of the same surface after two different exposures to [(fod)Ag(PMe₃)] at room temperature (B and C). The envelope of the C 1s spectrum of the polyurethane film has two maxima at 284.8 and 286.3 eV. This spectrum can be deconvoluted into six components at positions 284.5, 285.0, 285.8, 286.4, 287.8, and 289.3 eV which we can attribute to C=C, CH₂, =C–NH, C–O, C=O/C=N, and O–C=O, respectively.^{10,20} Successive exposure to the Ag complex leads to changes in the relative intensities of all C 1s peaks; the more apparent is a decrease in the intensity of the C 1s peak centered at 286.4 eV and the increase and shift to lower binding energy of the peak from 284.5 to 284.3 eV, indicating that the chemical environment of carbon is perturbed by the presence of Ag complex. Earlier work interprets this decrease in the intensity of these peaks (C–N, C–O, C=O, and O–C=O) after physical deposition of Ag films on polymer surfaces as the result of the removal of these functional groups from the surface; hot Ag atoms induce the dissociation of these groups.²¹ Our results, however, are obtained at room temperature, and the decrease in the intensity of these C 1s peaks after the adsorption of [(fod)Ag(PMe₃)] may be due to the formation of [(fod)Ag–O–C] and [(fod)Ag–N–C] species at the surface. The formation of these species probably induces a charge transfer to the carbon

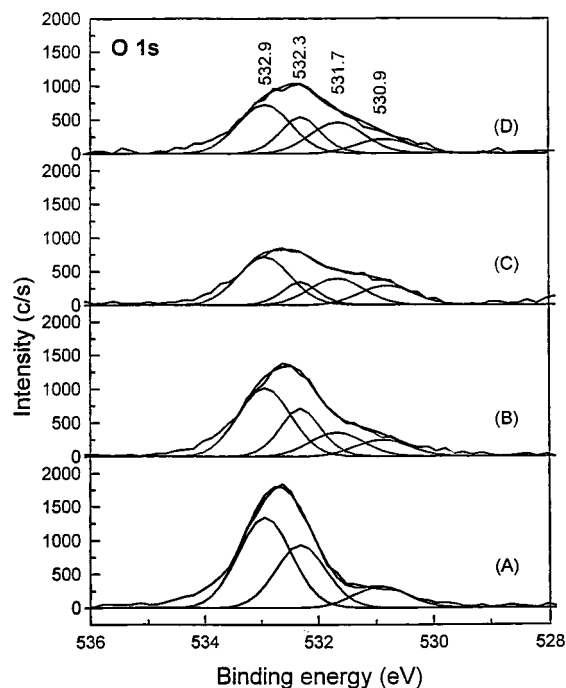


Figure 3. O 1s spectra of variously treated polyurethane spin-cast films: (A) polyurethane film on Al disk, (B) [(fod)Ag(PMe₃)]/polyurethane (1.8×10^5 langmuirs), (C) [(fod)Ag(PMe₃)]/polyurethane (2.8×10^5 langmuirs), (D) [(fod)Ag(PMe₃)]/polyurethane (3.9×10^4 langmuirs), exposed to HCHO. All exposures made at 300 K.

atoms through oxygen and nitrogen atoms. Thus, this decrease in the intensity is the result of a change in the chemical environment of carbon and not due to the removal of these functional groups (associated with these peaks) from the surface. In addition to the reaction between the Ag complex and the surface functional groups which lowers the intensity of C 1s peaks of these groups, the presence of Ag atoms on the surface also contributes to the decrease of C=C and CH₂ peaks due to a “screening effect”; photoelectrons ejected from carbon atoms are partially trapped by silver present on the surface. Such a decrease in the intensity of all components in an XPS spectrum has been observed in a number of metal/polymer systems.²²

O 1s and N 1s spectra shown in Figures 3 and 4 for the same conditions as Figure 2 support our conclusions regarding the formation of species that involve interactions of the precursor with O- and N-containing moieties at the polyurethane surface. Figure 3A shows that the polyurethane O 1s band can be fitted by three components centered at 532.9, 532.3, and 530.9 eV. The intensity of the latter component remains constant during the adsorption of the silver precursor, and its origin remains unknown, but could be related to additives such as antioxidants or lubricants. The other O 1s peaks at 532.9 and 532.3 eV correspond to C–O and C=O groups, respectively. The adsorption of [(fod)Ag(PMe₃)] leads to the emergence of a new peak at 531.7 eV, which we attribute to the formation of [(fod)–Ag–O–C] species at the polyurethane surface (Figure 3B,C). The intensity of this peak increases with increasing Ag precursor dose. Similarly, Figure 4 shows the N 1s region before and after exposure of the polyurethane to the silver complex. The N 1s region was also deconvoluted into two peaks at 400.0 and 398.4 eV. The former peak corresponds to the secondary amide [=C–N(H)–C=O] of polyurethane, whereas the latter might be attributed to the presence of imine groups such as [C=N], a minor constituent (10–15%). Exposure to [(fod)Ag(PMe₃)] leads to a decrease in the intensity of the higher BE peak and an increase in the intensity of the lower binding energy peak

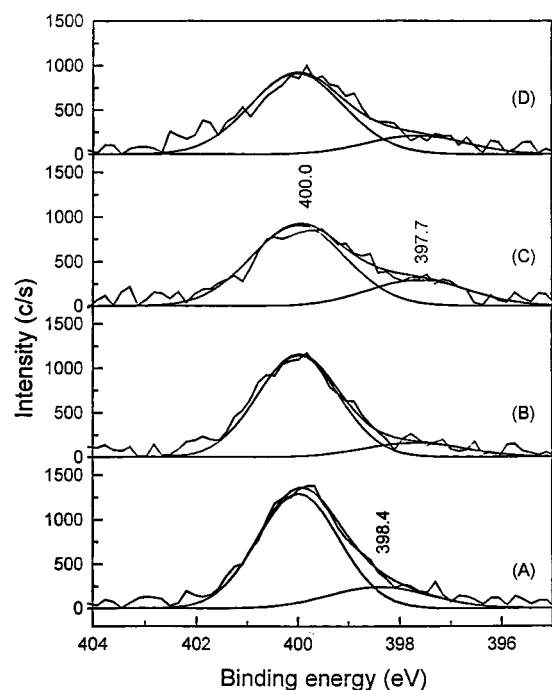
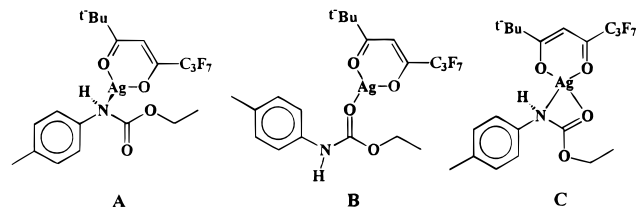


Figure 4. N 1s spectra of variously treated polyurethane spin-cast films: (A) polyurethane film on Al disk, (B) [(fod)Ag(PMe₃)]/polyurethane (1.8×10^5 langmuirs), (C) [(fod)Ag(PMe₃)]/polyurethane (2.8×10^5 langmuirs), (D) [(fod)Ag(PMe₃)]/polyurethane (3.9×10^4 langmuirs), exposed to HCHO. All exposures made at 300 K.

SCHEME 2: Model of the Complexes Formed in CVD Process between [(fod)Ag(PMe₃)] Precursor and Active Sites at a Polyurethane Surface



which is accompanied by a shift of the peak maximum from 398.4 to 397.7 eV, supporting the formation of a [(fod)Ag–N–C] entity.

Irreversible adsorption (reaction) of the Ag complex at room temperature can presumably only occur when the complex reacts with an active site such as NH, C–O–C, and C=O. At room temperature and above, all other (fod)Ag(PMe₃) precursor molecules will desorb. The present data indicate that adsorption of [(fod)Ag(PMe₃)] occurs with displacement of the [PMe₃] group and reaction with NH, C–O–C, and C=O functional groups, that is, by a ligand substitution reaction at the surface. Such a reaction would be similar to the displacement reaction which can take place in the gas phase between [(1,1,1,5,5,5-hexafluoropentanedionato)(1,5-cyclooctadiene)copper(I)], [(hfac)-Cu(COD)], and CO to yield [(hfac)Cu(CO)] species.²³ Scheme 2 shows what we believe (based on our RAIRS and XPS data) are the most probable chemical entities formed on the polyurethane surface at NH and C=O adsorption sites. Figure 5A,B shows F 1s spectra after the indicated exposures at room temperature and shows the expected increase with exposure. The F 1s BE at 683.9 eV is consistent with the presence of small fluorinated hydrocarbon fragments attached to a metallic surface.²⁴ It supports a hypothesis that involves the release of Ag atoms and the dissociation of a part of the fod ligand. The C 1s region, on the other hand, does not show any peak we can

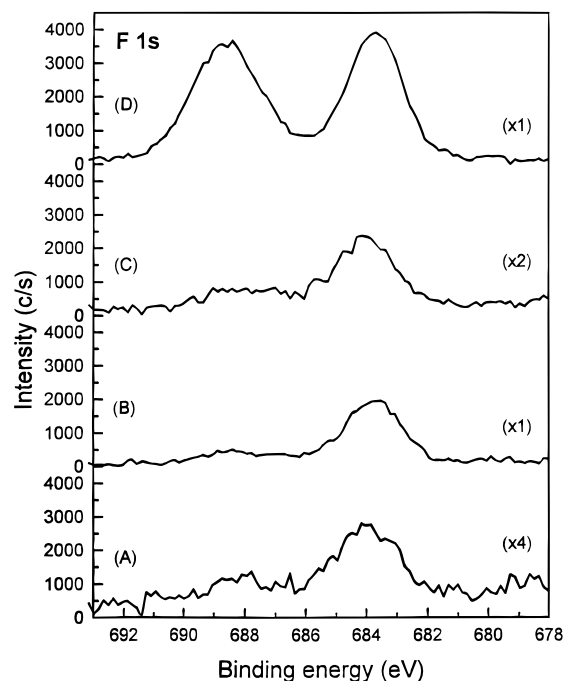


Figure 5. F 1s spectra of variously treated polyurethane spin-cast films: (A) [(fod)Ag(PMe₃)]/polyurethane (1.8×10^5 langmuirs), (B) [(fod)Ag(PMe₃)]/polyurethane (2.8×10^5 langmuirs), (C) [(fod)Ag(PMe₃)]/polyurethane (3.9×10^4 langmuirs), exposed to HCHO, (D) [(fod)Ag(PMe₃)] adsorption (9×10^4 langmuirs), after exposure to HCHO. All exposures made at 300 K.

attribute to the presence of CF₂ and/or CF₃ species on the surface. Taking into account the cross section and transmission function of the XPS spectrometer, which, to a first approximation, is proportional to the inverse of the kinetic energy, the C 1s peaks of fluorinated carbon of intact [fod] ligand should be approximately 20% of the intensity of the F 1s peaks. The absence of C 1s peaks related to fluorinated species is not due to the desorption of fluorinated fragments from the surface because the C 1s spectra were acquired before the F 1s spectra. Again, these data support the hypothesis that dissociation of the [fod] ligand is occurring. Spectra C and D of Figure 5 are described below.

Figure 6A,B shows the Ag 3d core level region after the indicated exposures to the silver precursor at room temperature. The intensities of the Ag 3d peaks increase as a function of exposure as expected. These data and those for HCHO-exposed surfaces (see below), spectra C and E in the inset of Figure 6, indicate a small shift (~ 0.1 eV) of the Ag 3d lines to lower BE with increasing coverage, although this is only just outside the reproducibility of the measurements. If the shift is real, it probably signifies the presence of bulklike Ag metal²⁵ as opposed to atomic Ag species. The Ag 3d data in the inset of Figure 6 are for a lower exposure of the precursor (D) and for a separate low exposure to the precursor, followed by HCHO (E). It is difficult to compare the absolute intensities of the Ag 3d peaks in these two experiments, but there is a trend toward higher Ag 3d intensity for samples treated with HCHO after the exposure to the precursor. Figure 7B,C shows the valence band region, as a function of exposure (Ag 4d band), and the width of the valence band indicates metallic character of the silver, possibly present as clusters.²⁵

B. Reaction of HCHO with [(fod)Ag–polyurethane] Complex. Unlike [Cu(I)(β -diketonate)] precursors, [Ag(β -diketonate)] complexes do not undergo a disproportionation reaction. For [Cu(I)(β -diketonate)] precursors this reaction leads

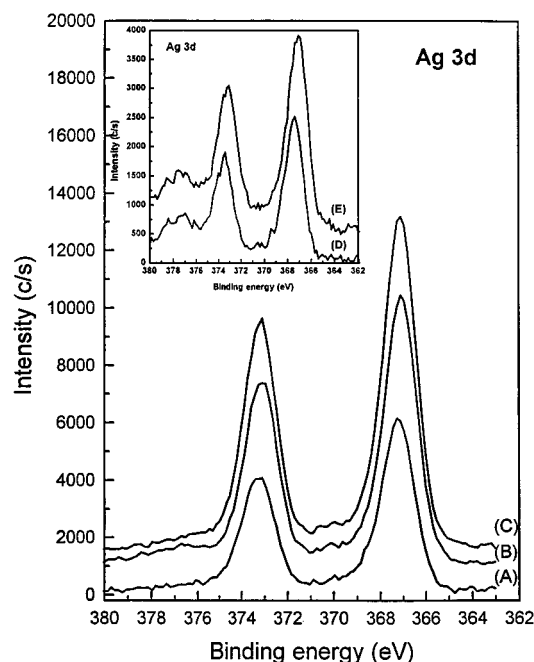


Figure 6. Ag 3d spectra of variously treated polyurethane spin-cast films: (A) [(fod)Ag(PMe₃)]/polyurethane (1.8×10^5 langmuirs), (B) [(fod)Ag(PMe₃)]/polyurethane (2.8×10^5 langmuirs), (C) [(fod)Ag(PMe₃)]/polyurethane (3.9×10^4 langmuirs), exposed to HCHO, with the Ag 3d spectra for low exposure given in the inset, (D) [(fod)Ag(PMe₃)]/polyurethane (6×10^4 langmuirs), (E) [(fod)Ag(PMe₃)]/polyurethane (3.6×10^3 langmuirs), exposed to HCHO. All exposures made at 300 K.

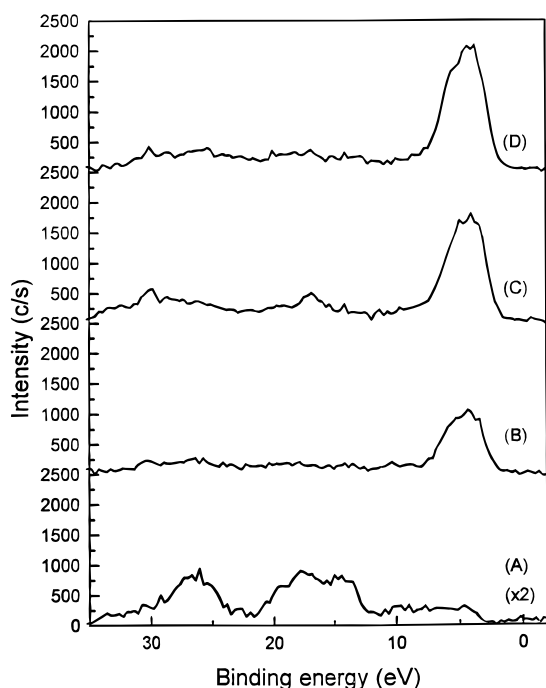


Figure 7. XPS data for the valence band region of variously treated polyurethane samples: (A) polyurethane film on Al disk, (B) [(fod)Ag(PMe₃)]/polyurethane (1.8×10^5 langmuirs), (C) [(fod)Ag(PMe₃)]/polyurethane (2.8×10^5 langmuirs), (D) [(fod)Ag(PMe₃)]/polyurethane (3.9×10^4 langmuirs), exposed to HCHO. All exposures made at 300 K.

to copper deposition and the desorption of volatile byproducts. Therefore, to maximize silver deposition, a second step is necessary, involving the reduction of Ag(I) to Ag(0), with the loss of the [fod] ligand. Polyurethane surfaces that had been exposed to the silver precursor were therefore further exposed

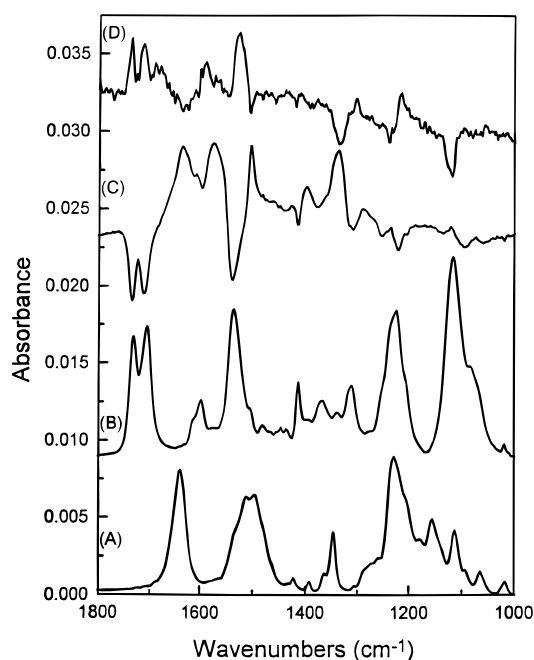


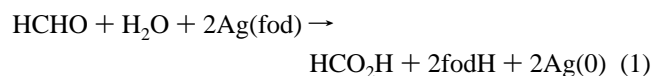
Figure 8. RAIR spectra of (A) [(fod)Ag(PMe₃)] in KBr disk, (B) polyurethane film on Al disk, (C) [(fod)Ag(PMe₃)]/polyurethane at 300 K (1×10^6 langmuirs), (D) [(fod)Ag(PMe₃)]/polyurethane (8.6×10^4 langmuirs), exposed to HCHO. Spectra c and D are difference spectra. See text for details.

to HCHO, a reducing agent. This reaction is a well-known reaction in the liquid phase (electroless plating) but as far as we know has not been attempted in an experiment involving sequential exposure of a surface to the reagents. Formaldehyde was adsorbed on the Ag-precursor-exposed polyurethane at different substrate temperatures to probe its reactivity toward adsorbed/reacted [(fod)Ag-polymer]. Figure 8 shows RAIRS results on samples that were first exposed to the silver precursor and then to [HCHO] at 323 K. The RAIR spectra of [(fod)Ag(PMe₃)]/polyurethane/Al and [HCHO]/[(fod)Ag(PMe₃)]/polyurethane/Al (Figure 8C,D) are the difference spectra, [(fod)Ag(PMe₃)]/polyurethane/Al is the background of the former spectrum, and [(fod)Ag(PMe₃)]/polyurethane/Al is the background of the latter spectrum. The negative peak at 1640 cm^{-1} indicates either that the (fod)–Ag bond breaks and the [fod] ligand is removed from the surface or that [HCHO] reacts with [fod–Ag] moiety to form a new volatile complex that is desorbed. On the other hand, the positive vibrational bands at 1730 , 1705 , 1537 , and 1226 cm^{-1} suggest that some of the adsorption sites are now free. Two explanations are possible for these positive peaks: (i) some [(fod)Ag] moiety was pumped out as the result of the interaction of [HCHO] with [(fod)Ag–O=C] species (or [(fod)Ag–O–C] and [(fod)Ag–N–C] species), leading to the formation of volatile species, or (ii) they are due to the possible formation of Ag clusters that free up sites on the polymer surface. If this latter mechanism is operative, it would be the microscopic basis of a continual increase in Ag coverage.

XPS results obtained after the postexposure of [(fod)Ag-polymer] to HCHO at room temperature are shown in Figures 2D (C 1s), 3D (O 1s), 4D (N 1s), 5C (F 1s), and 6C,E (Ag 3d). The C 1s, O 1s, and N 1s data show little change. Figure 5C shows a significant decrease of fluorine F 1s intensity without any loss of the Ag from the surface. The intensity of the Ag 3d peaks was higher in experiments in which the exposure of PU to the precursor was immediately followed by exposure to HCHO than for the cases where the PU was exposed solely to the precursor. (Figure 6C,E). This can be rationalized in the

following way. After exposure of the PU to the precursor, some precursor dissociates and some slowly desorbs. If this surface is immediately exposed to HCHO, some of the complex that had not yet desorbed is further reduced by HCHO, forming stable Ag species on the surface. Figure 5D shows F 1s data from a surface sequentially exposed to the precursor, HCHO, and then to more precursor, [(fod)Ag(PMe₃)]; i.e., the sequence of treatments from the last was [(fod)Ag(PMe₃)]/[HCHO]/[(fod)Ag(PMe₃)]/polyurethane/Al. Two F 1s peaks now appear at 683.9 and 688.5 eV, showing that there are two adsorption sites on the surface. The F 1s peak at 683.9 eV corresponds to fluorinated species such [C_xF_y] or [C_x(O)F_y] adsorbed on metallic sites and is the result of the dissociation of the precursor, whereas the F 1s peak at 688.5 eV corresponds to intact [(fod)Ag] fragments. This conclusion is based on our RAIRS and thermal desorption spectroscopy (TDS) studies of the adsorption of [(fod)Ag(PMe₃)] on Ag(111), which revealed deposition of Ag below room temperature and partial dissociation of the [fod] ligand.^{6–8} The F 1s spectrum in Figure 5D clearly indicates a similar interaction; i.e., after the treatment with HCHO, subsequently arriving [(fod)Ag(PMe₃)] is reacting with metallic Ag. The appearance of a high binding energy F 1s peak corresponding to the presence of intact [(fod)Ag] fragments is due mainly to the saturation of the surface of the Ag clusters and of active sites on the polyurethane surface with the silver complex. The inset of Figure 6 shows Ag 3d data for different exposures of silver precursor (Figure 6D), followed by HCHO exposure (Figure 6E). The amount of Ag increases with increasing exposure of both Ag precursor and HCHO. Also, there appears to be a significant shift in the Ag 3d peak to lower BE with HCHO exposure. In this case a maximum shift of the Ag 3d_{5/2} peak by 0.32 eV to lower binding energy was observed.

Reaction of Polyurethane with [fodH] and [HCHO]. To understand the mechanism of the silver deposition reaction and removal of [fod] ligand and its dissociation byproducts, polyurethane films were exposed to [HCHO] and [fodH]. RAIRS data revealed that both molecules have very low reactive sticking coefficients. Polyurethane films exposed up to 20 000 langmuirs of [fodH] at room temperature show no feature in the RAIR spectrum, indicating that [fodH] neither reacts with polyurethane surface nor is adsorbed at this temperature. On the other hand, the results of the adsorption of [HCHO] on polyurethane films showed that [HCHO] (720 langmuirs) interacts mainly with hydrogen-bonded carbonyl and N–H groups even at 325 K as shown in Figure 9 (the background is polyurethane/Al) by the decrease of the intensity of hydrogen-bonded carbonyl and δ-(N–H) vibrational bands and the increase of the intensity of free carbonyl band. This interaction, even if it is weak, may promote N–H bond dissociation. The overall reaction required for reduction of Ag(I) to Ag(0) by formaldehyde is shown in eq 1. There is sufficient water vapor in the ambient vacuum even at pressures of 5×10^{-9} to 1×10^{-8} Torr to account for this stoichiometry. The detailed mechanism on the surface cannot be determined, though it is reasonable to speculate that proton transfer from NH group to fod may be involved at intermediate stages. All of the proposed coordination modes A, B, and C of Scheme 2 will contain more acidic NH protons than in the free polymer, and so proton transfer to the [fod] ligand (and its dissociation byproducts) followed by the loss of [fodH] is not unexpected.



We also exposed the polyurethane surface to several thousand

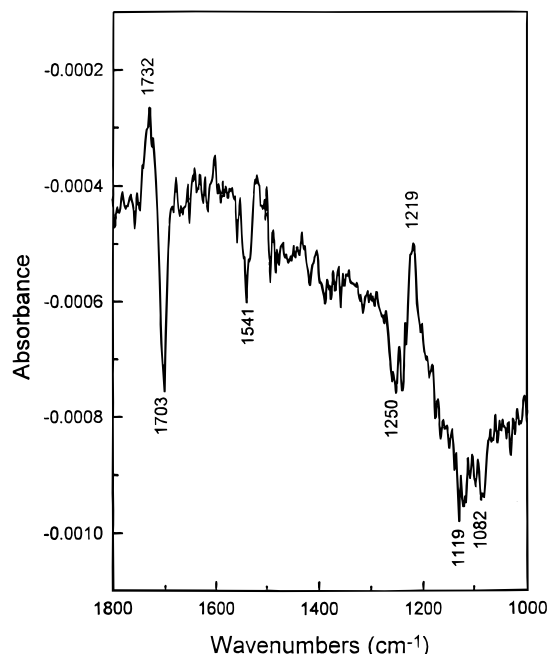


Figure 9. RAIR spectrum obtained after the adsorption of HCHO on polyurethane surface (720 langmuirs); the background is polyurethane/Al.

langmuirs of formic acid (HCOOH) at room temperature, but our IR studies shows that it does not react or adsorb. This provides evidence that any formic acid byproduct would desorb from the surface. The results show that the interaction of [HCHO] with [(fod)Ag–polyurethane] complex to remove the [fod] ligand is not a direct interaction between [HCHO] with [(fod)Ag], but it is mediated by polyurethane functional groups at the surface.

C. Atomic Force Microscopy of Silver Precursor Exposed Polyurethane Surfaces. Figure 10 shows a number of AFM images relevant to the present study. All topographic images are shown with the same vertical scale (correlated with height of the topographic features). Figure 10a shows a $5 \times 5 \mu\text{m}$ tapping mode topography image of a polished Al disk. Grains of aluminum oxide 100–300 nm in diameter and 20–100 nm in height are seen with several 20–40 nm deep grooves revealing the polishing direction. Figure 10b shows a $5 \times 5 \mu\text{m}$ tapping mode topography image of a thin film of polyurethane spin-coated on a polished Al disk. The polyurethane film here must be fairly thin (50 nm) since some topography of the substrate Al disk can still be seen, including aluminum oxide grains and two almost horizontal 5–10 nm deep polishing grooves. SFM phase images (not shown) of thin films of polyurethane spin-coated on Al disks revealed very small phase contrast ($<1^\circ$), indicating that the polymer film completely covers the Al surface. Figure 10c shows a $5 \times 5 \mu\text{m}$ tapping mode topography image of a polyurethane thin film after reaction with the silver complex. The presence of new small features on top of the polyurethane film is clearly seen as many small clusters with diameter of approximately 40 nm. Some larger features <500 nm in diameter are also seen which, based on the above observations, are attributed to aluminum oxide grains on the polished Al disk surface covered by polyurethane. These larger features are also partially covered by the new small clusters.

The three images in Figure 10d–f were recorded simultaneously (as described earlier) over the same area of the same sample shown in Figure 10c but with slightly higher magnification. Figure 10d shows a $2 \times 2 \mu\text{m}$ tapping mode topography

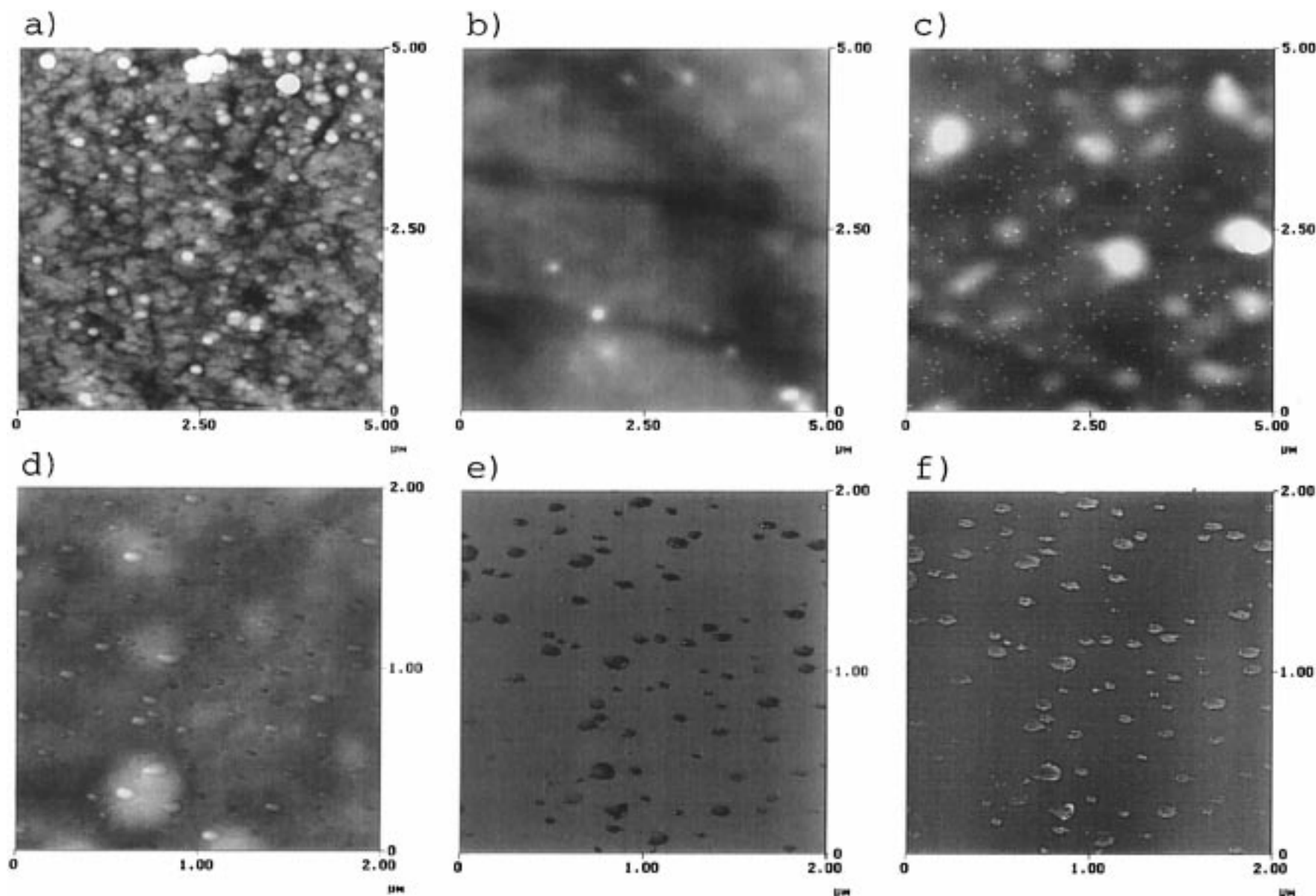


Figure 10. (a) A $5 \times 5 \mu\text{m}$ tapping mode image of polished Al disk (rms roughness is 9.6 nm; maximum height is 133 nm); (b) a $5 \times 5 \mu\text{m}$ tapping mode image of thin polyurethane film spin-coated on a polished Al disk (rms roughness is 5.6 nm; maximum height is 63.1 nm); (c) a $5 \times 5 \mu\text{m}$ tapping mode image of thin polyurethane film exposed to [(fod)Ag(PMe₃)] (rms roughness is 8.3 nm; maximum height is 164 nm); (d) a $2 \times 2 \mu\text{m}$ tapping mode image of thin polyurethane film exposed to [(fod)Ag(PMe₃)] (rms roughness is 3.5 nm; maximum height is 30.5 nm); (e) a $2 \times 2 \mu\text{m}$ phase mode image of thin polyurethane film exposed to [(fod)Ag(PMe₃)] (rms roughness is 0.9°; maximum height is 20.3°); (f) a $2 \times 2 \mu\text{m}$ amplitude mode image of thin polyurethane film exposed to [(fod)Ag(PMe₃)] (rms roughness is 0.5 nm; maximum height is 8.1 nm).

image. The presence of small clusters with a diameter of 50–100 nm on top of the spin-coated polyurethane film is obvious. Their heights are 2–5 nm. As in Figure 10b,c, the measured topography is still influenced by the roughness of the underlying Al disk surface. Figure 10e is a $2 \times 2 \mu\text{m}$ phase mode image. It shows two distinct areas with different phase lags. These areas are also obvious in the amplitude image mode (Figure 10f) and are located at almost the same positions. The acquired SFM phase and amplitude mode images (Figure 10e,f) of silver-exposed polyurethane film effectively remove most of the surface topography seen in Figure 10d. This indicates that the polished Al disk is completely covered by polyurethane. The small features of Figure 10d on top of polyurethane are also present in Figure 10e at approximately the same position. They exhibit substantial phase contrast (10–20° difference) consistent with a stiffer material than polyurethane in Figure 10e. We assign these features to silver clusters. These data provide direct microscopic evidence for the deposition of silver metal in the form of small clusters and so strongly support the conclusions made based on XPS evidence presented above.

Conclusions

We have reported on a study of the interaction of the silver precursor [(fod)Ag(PMe₃)] with polyurethane and the subsequent interaction of [HCHO] with adsorbed [(fod)Ag(PMe₃)]. The mechanism appears to involve a specific reaction between the Ag complex and the polyurethane functional groups (C=O, C–O–C, and NH). The use of [HCHO] as a reducing agent enhances the deposition of silver with concomitant loss of [fod] ligand and its dissociation byproducts from the polyurethane surface. RAIRS data revealed that the reduction of [(fod)Ag] complex with [HCHO] is mediated by functional groups at the polyurethane surface. Deposition of silver metal clusters can be achieved at temperatures well below the decomposition temperature of polyurethane. These observations, taken together with the possibility of non-line-of-sight coating, clearly demonstrate the feasibility of silver CVD on organic polymer substrates under mild conditions. The chief problem in developing a practical process is the relatively low volatility of the silver precursors which does not readily allow codelivery of the precursor and formaldehyde at the substrate. We suggest that an aerosol or other less conventional delivery system might be needed.

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