Plasma-Enhanced Chemical Vapor Deposited Phosphorus Sulfide Films. Characterization by Raman and Solid-State NMR Spectroscopies and Comparison to Melt-Quenched Glassy Materials

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Amorphous PS_x:H ($x \sim 1-7$) films have been synthesized, for the first time, from molecular H_2S and trimethylphosphine (TMP, $(CH_3)_3P$) precursors in an argon stream, using a plasma-enhanced chemical vapor deposition (PECVD) apparatus. The S/P ratio can be influenced by the H_2S/(TMP–)Ar flow-rate ratio during deposition. The molecular structure of these films has been compared to those of melt-quenched glasses and crystalline model compounds, using solid-state NMR spectroscopy and Raman scattering. In general, the atomic environments in the PECVD grown films are very similar to those observed in melt-quenched phosphorus sulfide glasses, including both polymerized $S=PS_{3/2}$ units, as well as molecular P_4S_7 and P_4S_{10}. No evidence was found for the formation of $PS_{3/2}$ type units, despite the use of a trivalent phosphorus precursor. This result indicates that, under the conditions of plasma synthesis and/or film deposition, phosphorus is oxidized to the pentavalent state.

Introduction

Non-oxide chalcogenide glasses based on the sulfides, selenides, and tellurides of main-group elements are solid-state materials of both technological and fundamental scientific interest.[1] Glassy SiS_2, $SiSe_2$, B_2S_3, and P_2S_5 form the base materials for a novel class of vitreous fast Li ion conductors with promise for solid-state battery applications.[2,3] They are also potentially useful in applications for infrared-transparent fibers and films.[4,5] From a scientific point of view, these amorphous homologues of glass-forming oxides are intriguing model systems to investigate fundamental questions concerning glass structure, a subject of much current interest. Most recently, such studies have produced intricate detail and structural insights into chalcogenide glasses, which frequently contradict long-held traditional views and concepts of glass structure.[6,7]

One of the general technological benefits of glasses (as opposed to crystalline compounds) arise from the wider opportunities of altering the physical properties of a chemical system in a continuous manner through compositional variation. In many oxide systems, nontraditional synthesis routes (sol–gel, chemical vapor deposition, etc.) have proven very useful for preparing homogeneous glasses in systems that would normally phase-separate under high-temperature melt conditions. In contrast to oxide glass systems, previous applications of nontraditional synthesis routes for non-oxide chalcogenide glasses have been extremely limited. Glassy As_2S_3 has been prepared by both solution-state process-

ing[8] and vapor deposition methods.[9] Plasma-enhanced chemical vapor deposition (PECVD) methods have been used for the preparation of amorphous $GeSe_2$ films.[10–12] In a more recent study, we have prepared amorphous SiS_2 films in this fashion, and characterized these materials structurally by Raman and solid-state NMR spectroscopies.[13]

Here we report the PECVD synthesis of amorphous materials in the phosphorus–sulfur system. This system was chosen because its overall structural evolution with increasing phosphorus content is highly unusual when compared to other group IV or V chalcogenide glass systems. Both Raman[14] and solid-state NMR spectroscopies[15] have shown that, at low P contents, the glass structures are based on polymerized $S=PS_{3/2}$ groups (containing pentavalent phosphorus) and sulfur chain units. A minor contribution from $PS_{3/2}$ groups (containing trivalent phosphorus) has also been inferred based on a Raman band near 420 cm^{-1}.[14] Above 20 at. % phosphorus, the structure becomes increasingly dominated by molecular P_4S_{10}, P_4S_9, and P_4S_7 units as the P/S ratio is increased. Preparations containing between 35 and 50 at. % phosphorus produce viscous liquids upon melt quenching, with subambient glass transition temperatures. NMR spectra of CS_2 extracts reveal these materials to be complex mixtures of molecular P_4S_n species ($10 \geq n \geq 3$).[15,16] Thus, as the P content of these glasses is increased, the dimensionality of the

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network increases initially, as the sulfur chain units are being cross-linked. Before a full 2-D network is established, however, the dimensionality of these glasses is reduced again as the introduction of further phosphorus leads to the formation of zero-dimensional P_4S_n molecular units.

The use of alternative preparation routes that bypass equilibration in the molten state may possibly result in materials that are structurally significantly different. Our work follows the single previous study known to us, reporting a solution-state precursor route.[17] Here, we demonstrate the preparation of amorphous phosphorus–sulfur films by PECVD methods and the possibility of adjusting the composition by the experimental conditions employed.

In terms of local structure, one could envision that the use of a trivalent phosphorus precursor such as trimethylphosphine (TMP) might favor the formation of $PS_{3/2}$ units instead of the $S=PS_{3/2}$ groups formed in the molten state. We are examining this question using both Raman and ^{31}P solid-state MAS NMR spectroscopic techniques. Previous NMR studies of binary phosphorus sulfides have shown that $PS_{3/2}$ and $S=PS_{3/2}$ groups each show wide variations in chemical shifts, resulting in substantially overlapping chemical shift ranges for both types of connectivity.[18,19] This complication may arise because all of the previous NMR data of phosphorus sulfides have been obtained on cage and ring compounds, where strain and bond angle variations may have a very large influence on ^{31}P chemical shifts. Therefore, we will discuss our results relating to P–S glasses and films in the context of new benchmark data obtained for noncage prototype model compounds, specifically $P(SC_6H_5)_3$ and $S=P(SC_6H_5)_3$, whose X-ray structures are known.[20–22]

Experimental Section

Sample Preparation. Bulk amorphous phosphorus sulfide glasses were prepared from the elements using standard literature procedures.[15] The a-PS_x:H samples were synthesized using a downstream plasma-enhanced chemical vapor deposition (PECVD) apparatus previously described.[13,23] In a typical deposition run an argon (Liquid Carbonic, chromatography grade) plasma was sustained (p_{Ar} = 900–1200 mTorr) by a 2.45 GHz Raytheon microwave power generator. Although the predominant phosphorus source used in the CVD literature is extremely toxic gaseous phosphine, in the present study liquid trimethylphosphine (TMP) was chosen for safety considerations and introduced into the gaseous state with an argon bubbler. TMP was synthesized from methylmagnesium iodide and triphenylphosphite in butyl ether.[24] After stirring

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Table 1. Representative Deposition Parameters for Amorphous PS_x Films and Results from Chemical Analysis (Flow-Rate Ratios of Hydrogen Sulfide and Argon/Trimethylphosphine Are Shown in Parentheses)

	sample					
	A (1:1)	B (2:1)	C (3:1)	D (3:1)	E (3:1)	F (4:1)
flow rate: H₂S:TMP/Ar (sccm)	150:150	150:75	210:70	210:70	150:50	160:40
deposit. pressure (mTorr)	1200	950	900	1000	900	1200
deposit. rate (mg/h)	ca. 60	ca. 60	ca. 60	ca. 60	ca. 60	ca. 60
MW power (W)	64	68	46	64	48	72
wt. % P	29.8	23.6	12.7	14.9	17.1	10.6
wt. % S	28.2	46.4	73.7	51.2	46.0	65.7
wt. % C	17.20	8.01	3.55	5.65	3.21	5.00
wt. % H	5.29	2.22	1.44	3.18	1.99	3.07
wt. % O			1.69			
calc stoichiometry PS_x	$PS_{0.9}{}^a$ $PS_{1.5}{}^b$	$PS_{1.9}{}^a$ $PS_{2.7}{}^b$	$PS_{5.6}{}^a$ $PS_{6.1}{}^b$	$PS_{3.3}{}^a$ $PS_{4.9}{}^b$	$PS_{2.6}{}^a$ $PS_{4.4}{}^b$	$PS_{6.0}{}^a$ $PS_{7.4}{}^b$

[a] From elemental analysis data for P and S. [b] From elemental analysis data for P, C, H, assuming S to be the residue.

the reaction mixture for 4 h, the product was distilled off (boiling point 39 °C). Identity and purity were checked by ^{31}P liquid-state NMR (single resonance, δ = 61 ppm vs 85% H_3PO_4). The reactant compounds TMP and H_2S were introduced into the downstream tail of an argon plasma and reacted to form amorphous films ca. 1–3 cm downstream of the plasma on an aluminum foil substrate and the silica walls of the plasma apparatus at room temperature. Deposition parameters are listed in Table 1. The sulfur/phosphorus ratios were altered by adjusting the $H_2S/(TMP-)Ar$ flow rate ratio within the range of 1–4. The deposits appeared visually homogeneous and ranged from brown to yellow-white. The films are extremely unstable in ambient conditions and are hydrolyzed rapidly by moisture, forming H_2S. Therefore, all sample handling and storage was done in a stainless steel glovebox sustaining a dry helium atmosphere with water levels less than 1 ppm.

The model compounds were prepared as follows.[25] $P(SC_6H_5)_3$: A 2.0 M PCl_3 solution in methylene chloride (Aldrich) was slowly added to a suspension of $NaSC_6H_5$ (prepared from Na and thiophenol (Aldrich, 97%, dried over P_2O_5 and vacuum distilled)) in thiophenol under an N_2 atmosphere at 22 °C. A slight excess (~10%) of $NaSC_6H_5$ was used. The mixture was filtered and the colorless crystals (plates) formed by slow solvent evaporation. The product was recrystallized from anhydrous diethyl ether; mp = 78.9 °C (lit. 77 °C); liquid-state ^{31}P NMR ($CDCl_3$ solution) singlet δ = 134.8 ppm.

$P(SeC_6H_5)_3$: A suspension of $NaSeC_6H_5$ in THF was prepared by the reduction of diphenyl diselenide (Aldrich, 98%) in THF by sodium metal.[26] To the suspension, 2.0 M solution of PCl_3 in methylene chloride (Aldrich) was slowly added. A slight excess (~10%) of $NaSeC_6H_5$ was used. The mixture was filtered and clear yellow crystals (hexagonal plates) were obtained by slow solvent evaporation and subsequently recrystallized from anhydrous diethyl ether; mp 96.4 °C (lit. 91–96 °C); liquid-state ^{31}P NMR ($CDCl_3$ solution) singlet, δ = 114.9 ppm. This compound easily oxidized to $O=P(SeC_6H_5)_3$; mp 110 °C; δ = 12.7 ppm on exposure to air.

$S=P(SC_6H_5)_3$: $SPCl_3$ (Aldrich, 98%) was slowly added to a suspension of $NaSC_6H_5$ in thiophenol (~10% excess) under an N_2 atmosphere at 22 °C. The mixture was filtered and colorless crystals (plates) formed by slow solvent evaporation at room temperature. This material was recrystallized from a 1:99 v/v mixture of thiophenol and diethyl ether; mp 88.8

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°C (lit. 86 °C); liquid-state ^{31}P NMR (CDCl₃ solution) singlet, $\delta = 91.3$ ppm.

Characterization. X-ray powder diffraction, carried out on a Scintag diffractometer using Cu Kα radiation, confirmed the totally amorphous character of all of the PS$_x$:H films prepared. Chemical analysis (Galbraith and Huffman Laboratories) gave the results listed in Table 1. It was found that the elemental contents frequently did not add up to 100%; however, oxygen analysis showed contents too low to account for this difference. Comparison with standards revealed that the sulfur contents were always underdetermined, suggesting that some of the sulfur is lost in the analysis procedure. Table 1 thus lists lower and upper limits for S/P ratios based on (a) the actual analytical results and (b) based on the analysis for P, C, and H, assuming the balance to be sulfur. The latter compositions appear to be more accurate based on the Raman spectroscopic results as discussed below. Regardless of the uncertainty thus associated with the exact chemical compositions of these films, it is clear that their P contents can be varied by the flow rate ratio in a fairly reproducible fashion. It is noteworthy that substantial amounts of carbon and hydrogen are incorporated into these films. For samples A and B the atomic H/C ratio lies near 3, consistent with the presence of methyl groups, while samples C—F show higher H/C ratios (between 4.9 and 7.4).

Raman spectra were recorded in a backscattering geometry using a liquid nitrogen cooled 2D CCD detector (Princeton Instruments Model LN/CCD-1152/UV) attached to a fast f/6.9 0.5 m monochromator (Acton Research Model Spectra Pro-500) equipped with 600 grooves/mm grating blazed at 500 nm. Approximately 5 mJ/pulse at 10 Hz of the 532 nm radiation generated by a Nd:YAG laser (Quanta Ray DCR-11) was softly focused onto the capillary Pyrex tube containing powdered sample. A Raman holographic edge filter (Physical Optics Corp., Model RHE 532.10) placed in front of the entrance slit of the monochromator provided overall 10^{-10} stray light rejection factor at 300 cm^{-1} from the Rayleigh line. Typical exposure time was 15 s. The accuracy of the measurements was better than 2 cm^{-1}. Due to limitations associated with utilizing small-size fast spectrometers for Raman scattering (filter cutoff), peaks below 400 cm^{-1} are substantially reduced in intensity.[27] This needs to be kept in mind when comparing our results with those in the literature.[14] Complementary infrared spectra were taken on KBr pellets of representative samples, using a Biorad FTS-60 FT-IR spectrometer, with 256 scans and 2 cm^{-1} resolution.

^{31}P magic-angle spinning (MAS) NMR experiments were carried out at 81.0 and 121.65 MHz, respectively, on Nicolet NT-200 and General Electric GN-300 spectrometers, equipped with a 7 mm multinuclear MAS-NMR probe from Doty Scientific. The following typical experimental conditions were used for ^{31}P MAS-NMR, in accordance with previous studies:[18] spinning speed 7 kHz, 90° pulses of 8–10 μs length, relaxation delay 10 min. Experiments with variable relaxation delays (up to 1 h) showed that these conditions result in representative peak area ratios. ^{1}H MAS-NMR spectra were recorded at 300.526 MHz on a General Electric GN-300 spectrometer at 300.526 MHz, using spinning speeds of 6–8 kHz, 2 μs pulse lengths, and relaxation delays of 4–8 min.

Results and Discussion

Raman Spectroscopy. Figures 1 and 2 compare the Raman spectra of bulk P—S glasses prepared by melt-quenching and of PECVD-grown amorphous P—S films. Peak maxima observed for both series of samples are listed in Table 2, which also includes assignments. The results obtained on the bulk P—S glasses are in good agreement with previous data by Koudelka et al.[14] The band at 471–480 cm^{-1} coincides with an intense band seen in the Raman spectrum of molecular S₈ and

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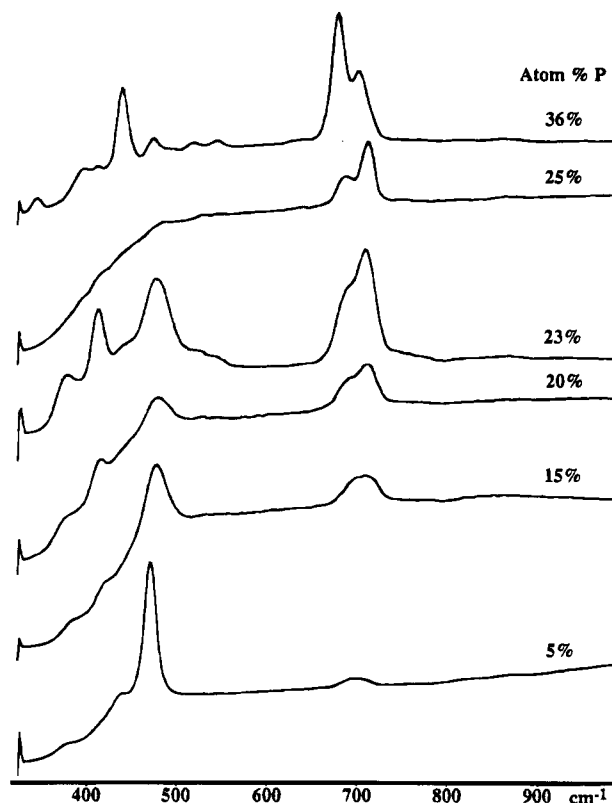
Figure 1. Raman spectra of bulk P—S glasses. Compositions are indicated in the figure.
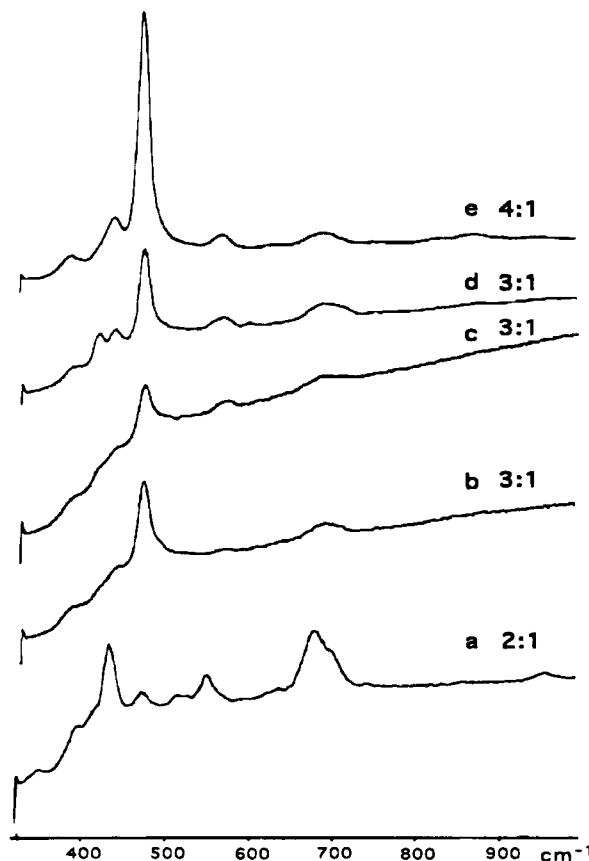
Figure 2. Raman spectra of amorphous P—S:H films, prepared by PECVD. H₂S/TMP—Ar flow rate ratios are indicated.

is assigned to the A₁ S—S stretching mode. Clearly, the intensity of this band decreases with increasing phosphorus content, indicating the successive depletion of
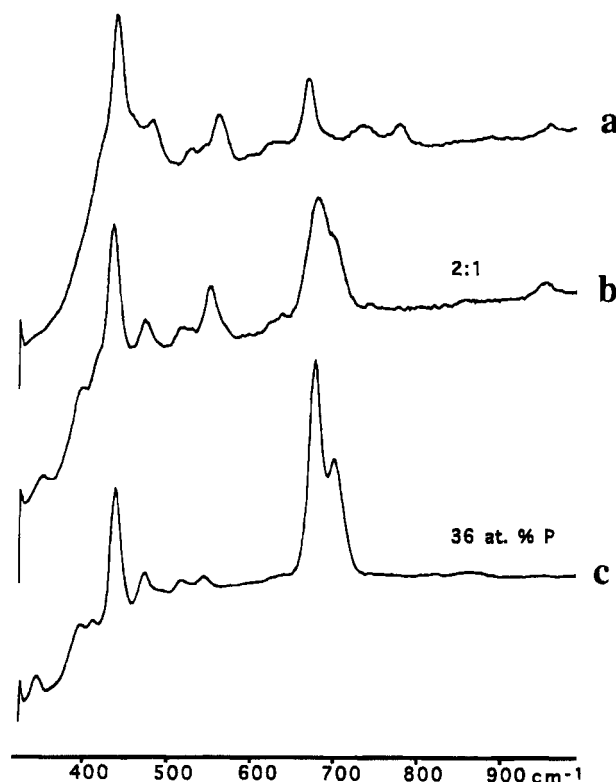
Table 2

(a) Raman Frequencies for PECVD-Grown PS$_x$ Films

freq (cm^{-1})	A (1:1)	B (2:1)	C (3:1)	D (3:1)	E (3:1)	F (4:1)	assignment
						387 w	
	443 s	438 s				438 w	A$_1$ P$_4$S$_7$
	484 m	476 w	470 s	473 m	472 s	471 s	A$_1$ S$_8$
	531 w	525 w					P$_4$S$_7$ and comb freq
	563 m	554 mw	566 w	569 w	567 mw	566 w	?
					598 w		
	672 ms	683 s	691 m	691 w	687 m	691 w	ν(P=S)
		699 sh					
	738 w						
	781 w						
		957 w					
					1399 w		

(b) Raman Frequencies Measured for Melt-Quenched Phosphorus Sulfide Glasses

freq (cm^{-1})	5% P	15% P	20% P	23% P	25% P	36% P	assignment
				415 m			ν(PS$_{3/2}$)
						441 m	A$_1$ P$_4$S$_7$
	471 s	480 m	480 m	480 s		475 w	A$_1$ S$_8$
				520 sh		519 w	?
				538 sh			
						546 w	B$_1$ P$_4$S$_7$
			695 sh	693 sh	689 m	680 s	ν(P=S)
	700 w	711 s	711 s	711 s	714 s	703 m	ν(P=S)

this structural fragment, and its final disappearance near 25 at. % phosphorus. In addition, all of the P–S glasses show a Raman scattering line near 415–420 cm^{-1}. On the basis of the observation that the intensity of this band increases with increasing phosphorus content, Koudelka et al. have assigned this band to a vibration involving a PS$_{3/2}$ structural unit.[14] Finally, the band near 700 cm^{-1} is unambiguously assigned to the stretching mode of the P=S double bond. As the phosphorus content is increased, the band becomes asymmetric and a developing maximum around 711–714 cm^{-1} is attributed to the formation of molecular P$_4$S$_{10}$ species, whose P=S stretching mode is known to appear around this wavenumber. The sample containing 36 at. % phosphorus shows fundamentally different Raman scattering lines, which are easily assigned to molecular P$_4$S$_7$ species (see below). The shift to 680 cm^{-1} of the P=S stretching mode in crystalline P$_4$S$_7$ is well documented[28] and possibly signifies a weakening of this double bond due to strong intermolecular interactions.[29] Figure 1 illustrates that the same holds true for amorphous P$_4$S$_7$. In addition, a second band appears at 703 cm^{-1}. This band is assigned to the P=S stretching modes in P$_4$S$_9$ and P$_4$S$_{10}$, both of which are identified in the NMR spectra (see below).

The Raman spectra obtained on the PECVD-generated samples and their dependence on the H$_2$S/(TMP−)Ar flow rate ratio used during synthesis are summarized in Figure 2. Aside from small peak shifts, the spectra are generally very similar to those of the bulk glasses at comparable compositions. As in the bulk glass series, the peak intensity ratio associated with the

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Figure 3. Comparison of the Raman spectra of (a) crystalline α-P$_4$S$_7$ (see text), (b) PECVD grown PS$_x$:H film, prepared at an H$_2$S/(TMP−)Ar flow rate ratio of 2:1, (c) melt-quenched glass containing 36 at. % phosphorus (based largely on amorphous P$_4$S$_7$).

S–S A$_1$ mode (470 cm^{-1}) and the P=S stretching mode (711 cm^{-1}) is correlated in the expected fashion with the S/P ratio and the H$_2$S/(TMP−)Ar flow rate ratio used in the synthesis of these films. The 415–420 cm^{-1} band assigned to PS$_{3/2}$ groups in the glasses has very weak intensity in the spectra of the PECVD grown films. Thus the Raman spectra show no evidence for an increased fraction of PS$_{3/2}$ groups in these materials.

While these results confirm that the PECVD method produces materials that are chemically very similar to the bulk glasses, the Raman spectra reveal specific differences between both groups of materials. For instance, all of the PECVD samples show an additional band within the range 554–569 cm^{-1}, which is not present in bulk phosphorus sulfide glasses, and may arise from hydrogen and/or carbon-containing sample contaminants. Other bands observed in some samples at wavenumbers >740 cm^{-1} are likely due to species formed in the presence of hydrogen or oxygen impurities. Sample A, containing the lowest S/P ratio, did not yield a Raman spectrum in the amorphous state, due to intense absorption of laser power. Upon crystallization of this sample in the laser beam, however, all of the characteristic lines of α-P$_4$S$_7$ are observed in the spectrum. Figure 3 compares this spectrum with those of sample B as well as a bulk glass containing 36 at. % phosphorus. Clearly, the latter two samples must be structurally extremely similar to each other, and Figure 3 suggests that both of these materials are largely composed of amorphous P$_4$S$_7$.

^{31}P MAS-NMR Spectroscopy of Model Compounds. Figure 4 shows the ^{31}P MAS-NMR spectra of the model compounds S=P(SC$_6$H$_5$)$_3$, P(SC$_6$H$_5$)$_3$, and
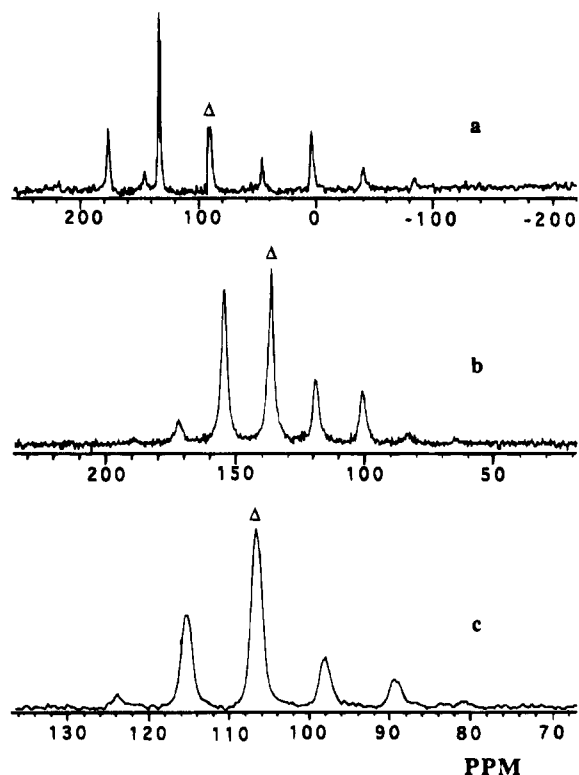
Figure 4. 121.65 MHz ^{31}P MAS NMR spectra of (a) S=P-(SC$_6$H$_5$)$_3$, (b) P(SC$_6$H$_5$)$_3$, and (c) P(SeC$_6$H$_5$)$_3$. Central resonances are marked by the symbol △.

Table 3. ^{31}P Chemical Shift Tensor Components (in ppm vs 85% H$_3$PO$_4$) for Crystalline Model Compounds

compound	δ_{iso} ($\pm$0.5 ppm)	δ_{33} ($\pm$5 ppm)	δ_{22} ($\pm$5 ppm)	δ_{11} ($\pm$5 ppm)
P(SC$_6$H$_5$)$_3$	135.9	88	157	163
S=P(SC$_6$H$_5$)$_3$	91.3	−90	182	182
P(SeC$_6$H$_5$)$_3$	106.6	89 ± 2	113 ± 2	118 ± 2

P(SeC$_6$H$_5$)$_3$. Table 3 summarizes the chemical shift tensor components, obtained by analysis of the spinning sideband intensities. Clearly, solid-state ^{31}P NMR is capable of distinguishing between S=PS$_{3/2}$ and PS$_{3/2}$ units in monomeric species. While both compounds have approximately axially symmetric ^{31}P chemical shift tensors, S=P(SC$_6$H$_5$)$_3$ has a much larger chemical shift anisotropy than P(SC$_6$H$_5$)$_3$ and the chemical shift tensor component measured along the S=P bond (−90 ppm) is at significantly lower frequencies than that measured along the 3-fold axis in P(SC$_6$H$_5$)$_3$ (+88 ppm).

^{31}P MAS-NMR Results of Melt-Quenched P−S Glasses. Figure 5 shows the ^{31}P MAS-NMR spectra of bulk phosphorus sulfide glasses as previously published.[15,16] At phosphorus concentrations ≤15 at. % the spectra are characterized by a broad asymmetric MAS central peak in the spectral region 90−115 ppm. On the basis of the anisotropic chemical shift parameters, this resonance has previously been assigned to S=PS$_{3/2}$ units within a polymerized matrix. There are at least three partially resolved spectral contributions to this line, their centers being located near −113, −106, and −95 ppm, respectively. In addition, a minor spectral contribution is found in the 140−150 ppm range. On the basis of the model compound data and the Raman results, we assign this feature to monomeric PS$_{3/2}$ units. Finally, these low-phosphorus glasses show a weak spectral contribution near 35 ppm. This observation is
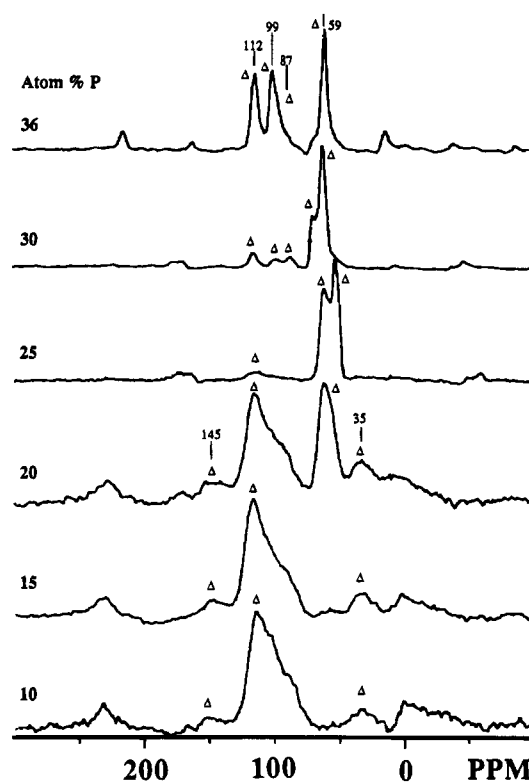
Figure 5. 81.0 MHz ^{31}P MAS-NMR spectra of melt-quenched P−S glasses. Central peaks are marked by the symbol △ and by the chemical shifts ($\pm$2 ppm) listed.

consistent with liquid-state NMR spectra of CS$_2$ extracted low-phosphorus glasses, which show the most intense resonance near this chemical shift. Demarcq tentatively assigns this resonance to a phosphorus persulfide type species.[30,31]

Glasses with phosphorus contents exceeding 15 at. % show additional sharp resonances in the 50−65 ppm range, which have been previously assigned to molecular P$_4$S$_9$ and P$_4$S$_{10}$ species.[15,16] The fraction of phosphorus atoms present within these molecules increases with increasing phosphorus content. Specifically, glass containing 36 at. % phosphorus shows two resonances at 112 and 99 ppm and a shoulder at 87 ppm, which are assigned to amorphous P$_4$S$_7$ in accordance with the literature.[32] In addition a sharp line at 59.1 ppm is observed, which is assigned to molecular P$_4$S$_9$. Samples with higher phosphorus contents are viscous liquid mixtures of P$_4$S$_n$ molecules at room temperature.

^{31}P MAS-NMR of PECVD Grown Films. Figure 6 shows the ^{31}P MAS NMR spectra of the PECVD grown films. Sample A (not shown) yields a broad feature centered near 80 ppm, a location not previously observed in either amorphous or crystalline phosphorus sulfide materials. Sample B (shown in Figure 7b) reveals a well-resolved spectrum with six distinct MAS central bands. The positions of the major peaks at 112, 97, and 84 ppm coincide closely with those measured in crystalline α-P$_4$S$_7$. Thus amorphous P$_4$S$_7$ is identified as the major component of sample B, in close agreement with the Raman studies. In addition, sample B shows resonances near 59 and 49 ppm, indicating the presence of P$_4$S$_9$ and P$_4$S$_{10}$, respectively. Finally, all of the

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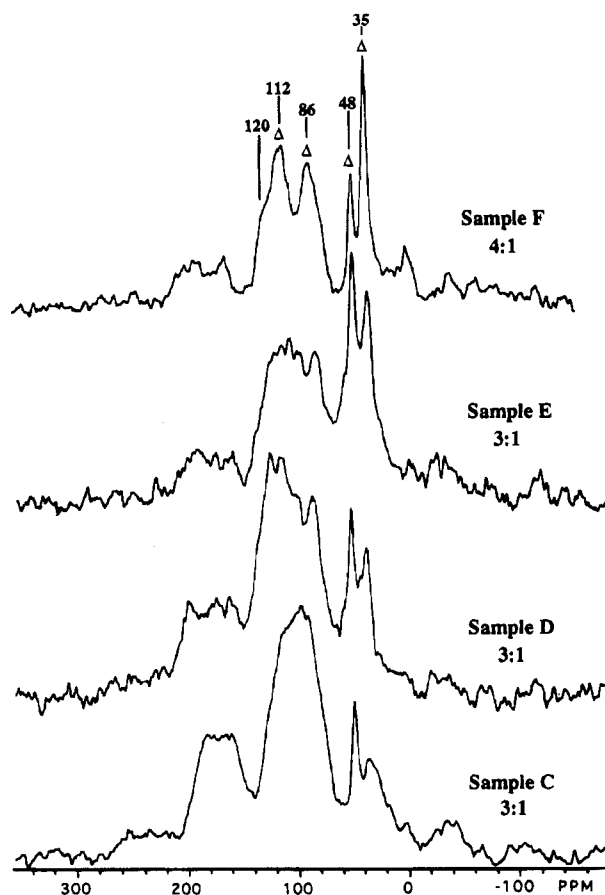
Figure 6. 81.0 MHz ^{31}P MAS-NMR spectra of PECVD-grown amorphous PS$_x$:H films. H$_2$S/(TMP−)Ar flow rate ratios are indicated in the figure. Central peaks are marked by the symbol △ and by the chemical shifts (±2 ppm) listed.

samples show the yet unassigned resonance near 35 ppm, albeit at far higher intensity than in the melt-quenched glasses.

Figure 7 illustrates interesting structural differences between a PECVD film and a bulk glass with similar elemental composition. While both samples contain largely amorphous P$_4$S$_7$, the MAS-NMR spectrum of the PECVD film shows a clear structural distinction between the two P-bonded phosphorus atoms P$_1$ and P$_2$, in close analogy to the situation in crystalline α-P$_4$S$_7$ (see Figure 7c). In contrast, this distinction is lacking in melt-quenched amorphous P$_4$S$_7$, in agreement with previously published work.[32] Thus, there appears to be a greater degree of site disordering in the latter material. While the lines are considerably broadened compared to the spectrum of α-P$_4$S$_7$, it cannot be ruled out that the PECVD grown material is in fact microcrystalline, with domain sizes too small to produce coherent X-ray scattering.

The ^{31}P MAS NMR spectra of samples C−F show multiple broad resonances with varying intensity distributions in the 85−125 ppm range as the dominant component. Spinning sideband patterns observed in slow spinning experiments and static wide-line spectra indicate an approximately axial chemical shift tensor with a large anisotropy and its unique component near −60 ± 20 ppm. On the basis of this spectroscopic information, the reference data of the present as well as previous studies, and the Raman spectroscopic results, all of these resonances are assigned to various
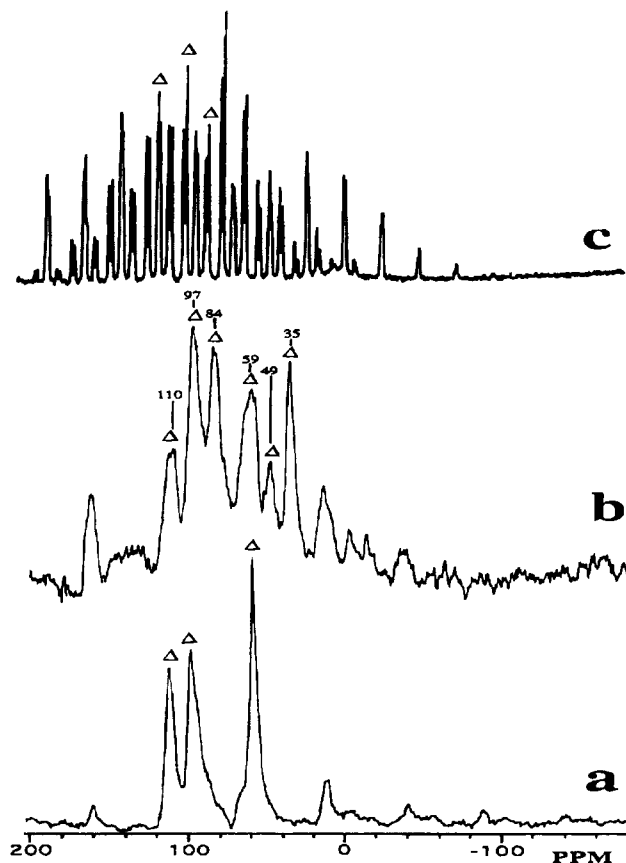

Figure 7. 81.0 MHz ^{31}P MAS-NMR spectrum of (a) P−S glass containing 36 at. % P, (b) of PS$_x$:H film prepared by PECVD, using an H$_2$S/(TMP−)Ar flow rate ratio of 2:1, (c) crystalline α-P$_4$S$_7$. Central peaks are indicated by the symbol △.

types of S=PS$_{3/2}$ units in different chemical environments. The spread in chemical shifts observed for these sites is probably caused by the distribution of hydrogen (and possibly carbon) and other types of defects in the vicinity of the phosphorus atoms. There is no clear evidence for the presence of PS$_{3/2}$ groups (no substantial spectral intensity in the 140−150 ppm range), despite the use of a trivalent phosphorus precursor in the PECVD procedure.

Additional minor spectral contributions for samples C−F are the 49 ppm line (tentatively assigned to molecular P$_4$S$_{10}$) and the 35 ppm peak, both of which have also been identified in sample B. The intensity of the 35 ppm line relative to the other peaks in the NMR spectra appears to be correlated with the relative intensity of the "extra" Raman band in the 560−570 cm^{-1} range, hence suggesting that both spectroscopic features arise from the same chemical species. It appears that this species is significantly more populated in the PECVD grown films than in the glasses. It is presently unknown whether the various P$_4$S$_n$ cluster species identified in the films and the glasses are molecularly dispersed throughout the glass matrix or whether they form separate microdomains. This question might be addressable by electron microscopy.

H-Containing Contaminants. Evidence from ^{1}H−^{31}P CPMAS, ^{1}H MAS NMR, and IR Spectroscopies. Attempts made for samples C and D to obtain ^{1}H−^{31}P CPMAS NMR spectra were unsuccessful. Thus, we have no evidence on whether both spin systems are dipolarly coupled and whether the P atoms
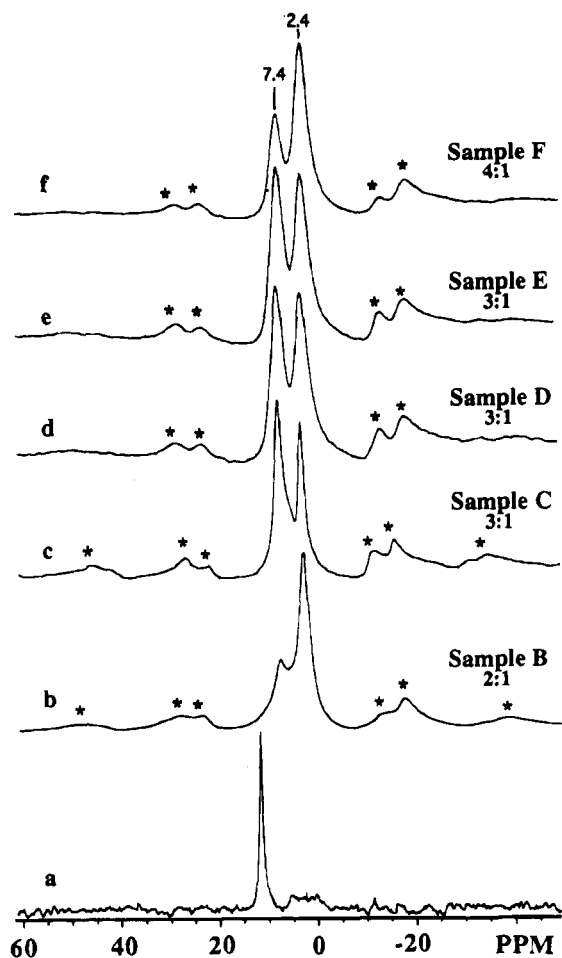
Figure 8. ¹H MAS-NMR spectra of (a) bulk P–S glass containing 15 at. % P and (b–f) PECVD grown samples B–F. Spinning sidebands are indicated by asterisks. Chemical shifts of the central peaks are shown in the figure.

are residing in the vicinity of hydrogen atoms. The absence of CP is consistent with the observation that the Raman and NMR spectra of the PS_x:H films are quite similar to the corresponding spectra of the melt-quenched glassy phosphorus sulfides. Nevertheless the line broadening observed in the ³¹P NMR spectra of the PECVD grown films suggests structural disorder which might be caused by the presence of hydrogen (and possibly carbon) bearing species in the vicinity of the P atoms. We cannot rule out that cross-polarization in this case is simply suppressed by molecular dynamics causing unfavorable relaxation characteristics. ¹H MAS-NMR results (see Figure 8) show two principal resonances near 7.4 and 2.4 ppm, respectively. Inspection of model compound databases[33] reveals that ¹H chemical shifts around 7 ppm are frequently observed for hydrogen atoms directly bonded to pentavalent phosphorus atoms. The 2.4 ppm resonance appears to be favored at low and at high S/P ratios, suggesting that it is comprised of multiple contributions. The ¹H chemical shifts of many types of methyl groups bonded to either tri- or pentavalent P atoms (in particular thiophosphoryl groups) resonate in the 2–3 ppm region.[34,35] In addition SHgroups might contribute to the 2.4 ppm resonance.
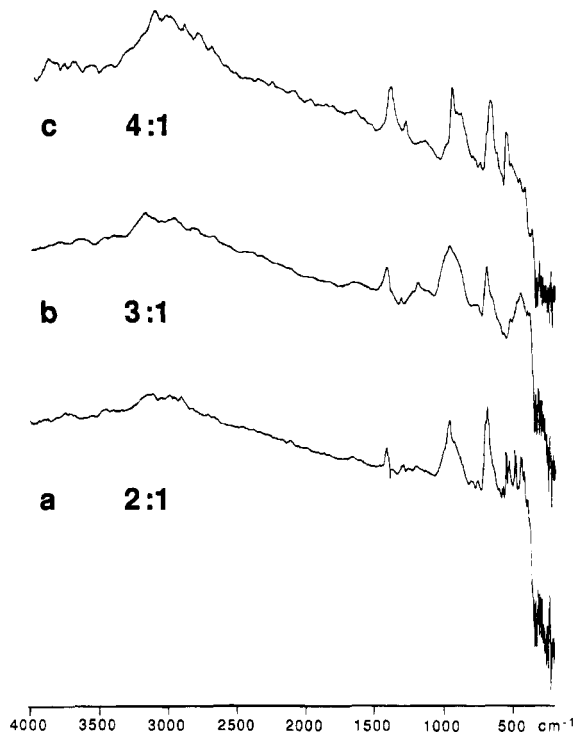
Figure 9. Infrared absorbance data of representative amorphous PECVD grown phosphorus sulfide films. a: sample B; b: sample C; c: sample F. Flow rate ratios are indicated.

Indeed, amorphous S:H films prepared by PECVD from H₂S alone show such a peak. On the other hand, in bulk P–S glass with comparable P content, hydrogen-bearing species arising from sample hydrolysis do not show this feature but rather yield a sharp peak near 11.2 ppm (assigned to P–OH groups).

Complementary IR studies of representative films (in KBr pellets) are shown in Figure 9. Interpretation of these spectra requires caution due to potential sample hydrolysis by residual moisture in the KBr. The spectra are quite similar to each other and show a strong broad absorbance near 3000 cm⁻¹ (C–H stretching mode, and O–H stretching mode due to water in KBr), a peak near 1400–1420 cm⁻¹, a weak sharp band at 1290 cm⁻¹, a broad band extending from 1000 to 890 cm⁻¹, probably arising from multiple contributions, and a band ranging from 710 to 680 cm⁻¹ (P=S stretching mode). The appearance of the two bands near 1290 and 890 cm⁻¹ can be taken as evidence for the presence of P-bonded methyl groups in accordance with data in the literature.[36,37] The 1420 cm⁻¹ band could stem from the C–H deformation mode, although it possesses unexpectedly high intensity. The band near 960–970 cm⁻¹ and the additional weak broad bands around 1700 cm⁻¹ and 1200 cm⁻¹ are consistent with O=P(OH) groups arising from sample hydrolysis.[37] There is also a weaker band near 550 cm⁻¹, whose relative intensity is correlated with that of the Raman band at 539 cm⁻¹. This suggests, that the corresponding mode is both Raman and IR active. In contrast to our tentative assignment of the ¹H MAS NMR spectra, the IR spectra show no clear evidence of P–H bonds (expected near 2350 cm⁻¹)

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or S—H bonds (expected near 2500 cm^{-1}). This might be explained by the fact that IR bands due to S—H bonds are generally weak, and also those of P—H bands can vary greatly in intensity.

Conclusions

The results of the present study show that amorphous phosphorus sulfide films bearing structural features similar to bulk phosphorus sulfide glasses can be prepared from trimethylphosphine and hydrogen sulfide by plasma-enhanced chemical vapor deposition. The S/P ratios of the films can be manipulated in the expected fashion by adjusting the flow-rate ratios of the reactant gases used. Amorphous P_4S_7 prepared by the PECVD method and by the traditional melt-quenching technique shows distinct structural differences in the local environments and ordering of the P-bonded phosphorus atoms. For all higher S/P ratios, however, the Raman and solid-state NMR results reveal that PECVD grown amorphous films are structurally very similar to the bulk glasses prepared, and consist largely of S—S

bonds, S=PS$_{3/2}$ groups, and molecular P_4S_7 and P_4S_{10} units. It is interesting to note that despite the use of a trivalent phosphorus precursor, the spectroscopic results do not show evidence for the presence of PS$_{3/2}$ groups in the PECVD-grown films. Evidently the molecular rearrangements occurring under plasma synthesis and/or film deposition conditions result in the oxidation of trivalent P atoms to pentavalent species. It might be possible to preserve the trivalent state on phosphorus if amorphous P—S materials are formed by solution-state metathesis reactions from suitable precursors.[17] Such reactions are currently under study in our laboratory.

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