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Local bonding configuration of phosphorus in doped and compensated amorphous hydrogenated silicon

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From an analysis of ^{31}P nuclear-magnetic-resonance spectra, the chemical nature and local bonding of phosphorus in samples of amorphous hydrogenated silicon (*a*-Si:H) have been determined. Overlapping spectra of threefold- and fourfold-coordinated phosphorus may be separated on the basis of dipolar couplings and identified on the basis of chemical shifts. At low concentrations of phosphorus, the ratio of threefold- to fourfold-coordinated phosphorus is approximately 4 to 1. The magnitudes of the ^{31}P-^{1}H and ^{1}H-^{1}H dipolar couplings indicate that fourfold-coordinated phosphorus is located at internal hydrogenated surfaces. Finally, the increase of fourfold-coordinated sites in compensated *a*-Si:H suggests the formation of boron-phosphorus complexes.

I. INTRODUCTION

The observation[1,2] that the electronic properties of tetrahedrally bonded amorphous semiconductors could be varied by many orders of magnitude by the incorporation of group-III and group-V impurities has led to many device applications. Nevertheless, the fundamental mechanism of doping and the electronic state of the dopant atoms is still somewhat uncertain. The empirical observation that large amounts of impurities (as compared to crystalline semiconductors) are required to shift the Fermi level led early workers[2-4] to assume that substitutional doping was occurring in materials which had high densities of intrinsic midgap states ($\gtrsim 10^{17}$ eV^{-1} cm^{-3}). Indeed, extended x-ray-absorption fine-structure studies of 1% arsenic-doped amorphous hydrogenated silicon (*a*-Si:H) showed that only $20 \pm 10\%$ of the As atoms were fourfold coordinated.[15] However, more recent investigations of electronic, optical, and structural properties of *a*-Si:H films have suggested other reasons for the ineffectiveness of the doping. First, ultraviolet-absorption studies in doped and undoped *a*-Si:H films suggest that the valence-band structure changes with the addition of either phosphorus or boron.[6] Second, deep-level transient spectroscopy (DLTS) measurements indicate that the density of midgap states in *a*-Si:H is only 10^{15} $eV^{-1} cm^{-3}$,[7] some 2 orders of magnitude lower than the early field effect and metal-oxide-semiconductor *C-V* measurements. Third, quantitative analysis of *a*-Si:H Schottky-barrier *C-V* measurements shows that only 1% of the phosphorus is electrically active,[8] although this value may be low owing to field-induced defect reactions. Fourth, several investigators[9-12] have noted that when small amounts of dopant are added there are significant changes in morphology and hydrogen distribution in *a*-Si:H films. Finally, combined composition, luminescence, optical, and electron-spin-resonance measurements have suggested recently[13] that doping introduces defects which "autocompensate" shifts in the Fermi level.

This paper presents an analysis based on ^{31}P nuclear magnetic resonance (^{31}P NMR) of the local bonding of phosphorus in doped and in compensated *a*-Si:H films. It is shown that the ^{31}P spectra associated with threefold- and fourfold-coordinated phosphorus may be identified on the basis of the chemical shifts. The relative intensities of the peaks give the distribution of threefold- to fourfold-coordinated

TABLE I. Details of sample compositions. Samples prepared with surface temperature of 275 °C, 1.5 W rf power (total), and 0.2 Torr total pressure.

Sample	mol %PH_3 in gas phase	mol %P in deposited film[a]	Conductivity $[(\Omega\ cm)^{-1}]$ at room temperature
A	1.0	1.8	1.5×10^{-2}
B	0.1	0.33	1.5×10^{-2}
C	0.5 ($0.5\% B_2H_6$)	0.16	1.7×10^{-6}

[a] As determined by ion microprobe analysis.

sites as typically 4 to 1, for films containing 1.8 to 0.3 mol % phosphorus. In addition, from the strengths of the heteronuclear dipolar couplings, it is shown that threefold-coordinated phosphorus is bonded to three Si atoms, and fourfold-coordinated phosphorus, which exists as either $P(Si-)_3H$ or $P(Si-)_3Si(H)$, is situated at internal hydrogenated surfaces. The spectrum of compensated *a*-Si:H suggests the formation of complexes of phosphorus and boron. These results are discussed in relation to the mechanism of doping in these technologically important materials.

II. EXPERIMENTAL PROCEDURES

The samples were prepared in a capacitively coupled radial flow deposition system with 6-in.-diam. electrodes. Table I details the preparation conditions, room-temperature conductivities, and the phosphorus content obtained by ion microprobe analysis. The samples were grown for 24—36 h resulting in sample masses of 0.3—0.5 g after removal of the aluminum substrates with a dilute acid etch. Inspection of infrared reflection measurements prior to removal of the film from the substrate showed no Si-O absorption modes.

^{31}P NMR data were obtained on a Bruker CXP-200 and an IBM instruments NR-80 spectrometer operating at 81.02 and 32.38 MHz, respectively. Most spectra were obtained by Fourier transforming a quadrature-detected free-induction decay (FID) accumulated by cosubtraction of the signals observed after a 90° pulse and $180°$-τ-$90°$ pulses. The delay τ was set longer than the spin-spin relaxation time, T_2, and shorter than the spin-lattice relaxation time, T_1. The spectra are plotted relative to ^{31}P in 85% H_3PO_4, such that downfield resonances lie to the left. In some cases the spectrum was measured by Fourier-transforming the echo following a spin-echo pulse sequence ($90°$-τ-$180°$-τ-echo). The intensity of the echo as a function of τ was used to determine T_2. In most experiments 1000 to 6000 averages were accumulated, with care taken to avoid artifacts caused by saturation of the ^{31}P magnetization.

III. RESULTS AND DISCUSSION

The phosphorus contents of the samples, shown in Table II, calculated from the calibrated intensities of the NMR spectra are in reasonable agreement with the results from the ion microprobe analyses. The T_1's of ^{31}P in *a*-Si:H are approximately 25 sec for all of the samples described in Table I. For ^{31}P in crystalline Si, at concentrations 2 orders of magnitude less than the samples studied here, the T_1's are approximately 0.1 sec at 1.3 K.[14] The short relaxation times in the crystalline Si were attributed to interactions with conduction electrons, known as the Knight shift,[15] and the relaxation times would therefore be predicted to be much shorter at 298 K. The long relaxation times and relatively small shifts in the spectra of ^{31}P in amorphous Si:H, shown in Fig. 1, indicate that interaction with conduction electrons does not dominate.

The spectra shown in Fig. 1 are relatively broad and slightly asymmetric. The line shapes are virtually unchanged[16] when observed while spinning the samples at 4.0 kHz at the "magic angle."[17] Thus the principal cause of broadening and asymmetry is not chemical shift anisotropy,[18] Knight-shift, or susceptibility effects.[19]

The nature of the broadening in the spectra in Fig. 1 can be further classified by the spin-echo experiment. In general, the intensity of a spin echo decays at a rate proportional to the homogeneous contributions to the linewidths of the constituent peaks

TABLE II. Analysis of ^{31}P NMR spectra.

		Threefold sites			Fourfold sites		
Sample	mol %P[a]	Mole fraction (%)	Center of mass[b] (±5 ppm)	Linewidth[c] (±5 ppm)	Mole fraction (%)	Center of mass[d] (±10 ppm)	Second moment[e] (G^2)
A	1.72	77	175	58	23	70	29±1.0
B	0.21	79	175	58	21	70	29±1.0
C		33	175	61	67	85	5.9±0.2
A (after anneal)	1.68	84	174	54	16	70	1.9±0.2

[a] Calculated from spectral areas calibrated with samples of InP and GaP.

[b] Relative to 85% H_3PO_4.

[c] Halfwidth at half-maximum height of the fitted Lorentzian function.

[d] As obtained by fitting a Gaussian function to the peak.

[e] For a Gaussian ^{31}P line shape, 29 G^2 corresponds to a halfwidth at half-maximum height 11 kHz, or 140 ppm.

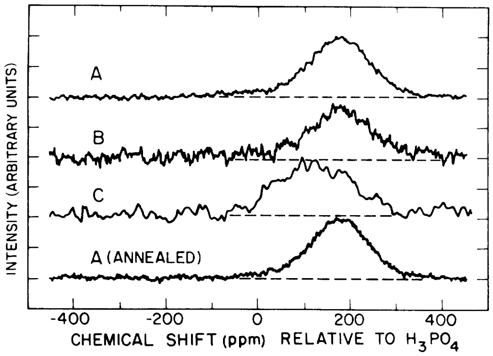

FIG. 1. ^{31}P NMR spectra at 295 K of the samples described in Table I. Spectra of samples A, B, and A (annealed) were measured at 81.02 MHz. The spectrum of sample C was measured at 32.38 MHz. A (annealed) was measured after sample A was heated to 750 K for one hour.

of a NMR spectrum. Broadening arising from chemical heterogeneity and chemical shift anisotropy in a rigid sample is inhomogeneous and will not contribute to the decay of the echo. The principal sources of homogeneous broadening in the ^{31}P spectrum are homonuclear dipolar couplings to other ^{31}P nuclei and heteronuclear couplings, especially to ^{1}H nuclei. The ^{31}P nuclei in a-Si:H constitute a dilute spin system (for example, in sample A, only $\sim 2\%$ of the silicon sites are occupied by phosphorus) and thus, ^{31}P-^{31}P couplings will cause the intensity of the spin echo to decay exponentially with τ (Lorentzian). Moreover, because of the large dispersion of ^{31}P chemical shifts relative to the dipolar linewidths, the x and y components of the phosphorus magnetizations are decoupled and the ^{31}P-^{31}P dipolar interaction is heteronuclear. The time constant for the decay is determined by the concentration and distribution of ^{31}P in the lattice and in the case of a random distribution, the time constant in msec is $0.18c^{-1}r^3$ where c is the mole percent and r is the Si-Si internuclear distance, ~ 2.35 Å.

The effect of heteronuclei, such as ^{1}H, on the decay of the ^{31}P spin echo is determined by the strength of the ^{31}P-^{1}H and ^{1}H-^{1}H dipolar couplings. The intensity of the echo can be calculated from the distribution of phase angles of the ^{31}P nuclear magnetic vectors at the time of the echo, analogous to the approach used to calculate the effects of diffusion through a magnetic field gradient.[20] The intensity of the ^{31}P echo at time 2τ is

$$M(2\tau)=M(0)\int_{-\infty}^{\infty} P(\Phi)\cos\Phi\, d\Phi \tag{1}$$

where $M(0)$ is the intensity of the spectrum measured as a FID and $P(\Phi)$ is the probability distribution function of ^{31}P phase angles, Φ. The rate of precession of the phase of the ^{31}P magnetization is proportional to the z components of the neighboring ^{1}H nuclei, $S_{z,k}$. The accumulated phase of a ^{31}P nucleus i at the time of the echo is

$$\Phi_i(2\tau)=\sum_k a_{i,k}\left[\int_0^{\tau} S_{z,k}(t)dt-\int_{\tau}^{2\tau} S_{z,k}(t)dt\right], \tag{2}$$

where $a_{i,k}$ is the dipolar coupling between ^{31}P-^{1}H pairs in rad sec^{-1}. The probability distribution for S_z can be obtained from the ^{1}H NMR line shape, which is Gaussian for clustered ^{1}H nuclei in a-Si:H.[21] Thus the probability distribution function of Φ is also Gaussian,[20]

$$P(\Phi)=(2\pi\langle\Phi^2\rangle)^{-1/2}\exp(-\Phi^2/2\langle\Phi^2\rangle), \tag{3}$$

which when inserted into Eq. (1) yields

$$M(2\tau)=M(0)e^{-\langle\Phi^2\rangle}. \tag{4}$$

For a system of concentrated z spins (e.g., ^{1}H nuclei), the correlation function of S_z is exponential,[15] which may be represented as

$$\langle S_{z,k}(t)S_{z,j}(t+t')\rangle=\delta_{kj}e^{-|t'|/\tau_c} \tag{5}$$

which neglects concerted ^{1}H-^{1}H spin flips. The correlation time, τ_c, is approximated by $T_{2,S}$, the spin-spin relaxation time of the ^{1}H nuclei. Finally, upon substituting (5) into (2) and integrating,

$$\langle\Phi^2\rangle=\frac{2T_{2,S}^2}{(T_{2,IS})^2}\left[2\left[\frac{\tau}{T_{2,S}}\right]+4e^{-\tau/T_{2,S}}-e^{-2\tau/T_{2,S}}-3\right], \tag{6}$$

where $T_{2,IS}$ is the time constant of the ^{31}P-^{1}H coupling; $T_{2,IS}=2\pi\langle a_{i,k}^2\rangle^{-1/2}$.

The effect of ^{1}H nuclei on the decay of the ^{31}P echo can be calculated from Eqs. (4) and (6). In the limits $T_{2,S}\gg\tau$ and $T_{2,S}\ll T_{2,IS}$, $\langle\Phi^2\rangle$ approaches zero and $M(2\tau)\approx M(0)$, which predicts that the ^{1}H nuclei have a negligible effect. These limits are commonly known as isolated I-S pairs and self-decoupling, respectively. However, for $\tau>T_{2,S}$, $\langle\Phi^2\rangle$ approaches $4T_{2,S}\tau/(T_{2,IS})^2$ and the decay of the ^{31}P echo is exponential with a time constant of $\sim(T_{2,IS})^2/(4T_{2,S})$.

The spectrum observed as an echo with $\tau=0.25$ msec, shown in Fig. 2, decreased in intensity only 30% relative to the FID. Thus the principal source of the broadening is inhomogeneous, probably resulting from a distribution of isotropic ^{31}P chemical shifts, typical of amorphous materials. For example, similar distributions of the isotropic ^{29}Si chemi-

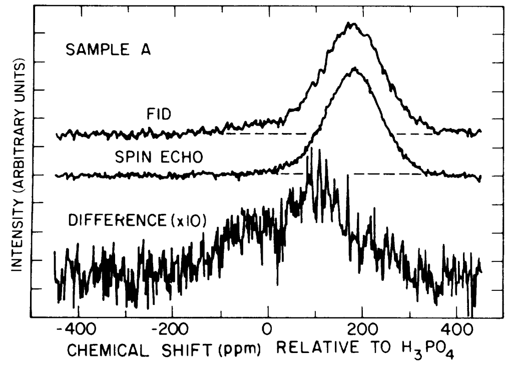

FIG. 2. ^{31}P NMR of sample A obtained from a FID and from an echo observed with $\tau=0.25$ msec, multiplied by 1.4 to compensate for the decay during the echo. The difference spectrum (× 10) was calculated by subtracting the normalized echo from the FID.

cal shifts have been reported.[22,23] By careful comparison of the spectra obtained as a FID and as an echo, it is noted that the downfield shoulder has vanished in the echoed spectrum (Fig. 2). The difference is emphasized by subtracting the two spectra, which yields the broad line shape shown in the bottom of Fig. 2. This difference line shape corresponds to ^{31}P species with a T_2 much shorter than the echo time, 0.5 msec.

The spin-echo experiment has revealed that the spectrum of sample A is the superposition of two line shapes with different T_2's. The spectrum of the species with the longer T_2 is fitted with a Lorentzian function of halfwidth 58 ppm, centered at 175 ± 5 ppm. The broad difference spectrum is best fitted with a Gaussian line shape centered at 70 ± 10 ppm, with a second moment of 29 G^2. (The artifact in the difference spectrum near 20 ppm is due to a dc offset in the decay.) The isotropic chemical shift and dipolar contribution to the broadening of each peak can be used to determine the chemical nature and local bonding of ^{31}P in a-Si:H, as follows.

To interpret chemical shift data, one must compare with values of known reference compounds, usually liquids, since it is not possible to calculate the shifts *a priori.* The best analogs for phosphorus in a-Si:H for which the chemical shifts have been measured are $P[Si(CH_3)_3]_3$ (251 ppm) and $PH[Si(CH_3)_3]_2$ (237 ppm).[24] There are no reported measurements on compounds which could serve as analogs for fourfold-coordinated phosphorus. However, it is generally observed that upon changing from triply bonded to quadruply bonded phosphorus, as with PR_3 to PR_4^+ (R is an aliphatic hydrocarbon) the ^{31}P chemical shift moves downfield, by 50—85 ppm.[24] On this basis, we assign the peak at 175 ± 5 ppm to threefold-coordinated phosphorus and the peak at 70 ± 10 ppm to fourfold-coordinated phosphorus.

The distribution of sites in each sample can be calculated by decomposing each spectrum in Fig. 1 into the sum of a Lorentzian function and a broad Gaussian on the downfield shoulder. The results of a least-squares fit to each spectrum are given in Table II. For both 1.8 mol % and 0.33 mol % P (samples A and B) the ratio of threefold- to fourfold-coordinated phosphorus is about 4 to 1.

The chemical shift of phosphorus can be used to distinguish between threefold- and fourfold-coordinated phosphorus, but it is relatively insensitive to the nature of the species bonded to the phosphorus (i.e., Si or H), compared to the total linewidth. For example, the ^{31}P isotropic shifts of $P[Si(CH_3)_3]_3$ and $PH[Si(CH_3)_3]_2$ differ by only 14 ppm.[24] The strength of the dipolar interaction, however, provides a direct measurement of the number of and distance to nearby magnetically active nuclei. Potential contributors to the dipolar broadening of the ^{31}P NMR spectrum include ^1H, ^{29}Si, and ^{31}P and in the compensated sample, ^{10}B and ^{11}B. Contributions to the ^{31}P spectra from ^{29}Si, ^{10}B, and ^{11}B may be neglected, because the systems are isotopically and chemically dilute, respectively, which results in long values of $T_{2,IS}$ and $T_{2,S}$, respectively. The strength of the ^{31}P-^{31}P and ^{31}P-^1H dipolar couplings for each site can be estimated from the linewidths via the Van Vleck equation,[15] and from the values of T_2 determined from the spin-echo experiment.

The decay of the intensity of the echo for the peak centered at 175 ppm, as a function of τ, is shown in Fig. 3. From the slope of the line through the data, the T_2 of this peak is 1.5 msec. Also, the decay is exponential, which is typical of coupling to a dilute spin system.[15] The decay of the magnetization of the threefold-coordinated phosphorus site can be accounted for by ^{31}P-^{31}P dipolar coupling.

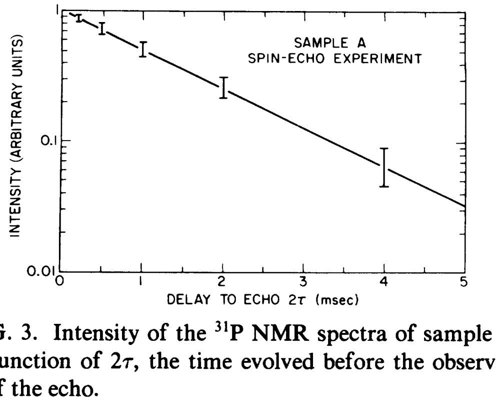

FIG. 3. Intensity of the ^{31}P NMR spectra of sample A as a function of 2τ, the time evolved before the observation of the echo.

For example, a random distribution of phosphorus at 1.72 mol %, with a large chemical dispersion, would yield a T_2 of 1.4 msec. The reciprocal of T_2 places a lower limit on the dipolar coupling at the threefold-coordinated site; i.e., the dipolar coupling is at least 670 Hz. This is only a lower limit because if the phosphorus were strongly coupled to a heteronucleus (e.g., bonded to a hydrogen atom) and the heteronucleus were spatially isolated from its spin system ($T_{2,S} \gg \tau$), the heteronuclear dipolar interaction would be refocused by the spin-echo experiment as discussed previously.

To test for heteronuclear coupling to ^{1}H, typically one would irradiate the sample at the resonant frequency of ^{1}H and observe whether the ^{31}P spectrum had narrowed. This approach proved to be impractical since the relatively high conductivity of the samples caused arcing during the comparatively long decoupling pulses (1—10 msec). Instead, the line broadening caused by hydrogen was removed by removing the hydrogen. Sample *A* was held at 750 K for 1 h, which has been demonstrated to remove most of the hydrogen from amorphous silicon.[25] The peak at 175 ppm in the spectrum of the annealed sample shown in Fig. 1, has not changed relative to the initial spectrum. Thus we attribute the broadening in the spectrum of the threefold-coordinated phosphorus to chemical inhomogeneity and *not* heteronuclear dipolar coupling. The threefold-coordinated phosphorus is therefore bonded to three Si atoms, which contribute about 160 Hz (5 ppm) to the linewidth.

The peak at 70 ppm is considerably broader than the peak at 175 ppm. If it is assumed that the contribution from chemical inhomogeneity is the same at each site, then the remainder of the second moment of the peak, 27 G^2, is the result of dipolar broadening. This corresponds to a dipolar coupling of about 8.9 kHz. The magnitude of T_2 for the fourfold-coordinated site could not be determined accurately from the spin-echo experiment because of its weak intensity and the fast decay of the echo. However, it is observed that the side peak has essentially vanished at $\tau = 0.25$ msec, which suggests that $T_2 \leq 0.20$ msec. After the hydrogen is removed from sample *A*, the peak at 70 ppm is considerably narrower and slightly decreased in intensity. The observations from the linewidth, spin-echo spectra, and annealed sample are consistent with a fourfold-coordinated phosphorus site in close proximity to clustered hydrogen (<2 Å). For example, the second moment of a spectrum of ^{31}P bonded to ^{1}H is calculated from the Van Vleck equation to be 19 G^2. The remainder of the broadening can be attributed to the other ^{1}H nuclei in the local cluster, as will be shown. The ^{31}P-^{31}P coupling in a small cluster of phosphorus (i.e., 5.7 G^2 for three phosphorus atoms) is weaker than the observed broadening. Although small phosphorus clusters may exist, they must be in the presence of hydrogen atoms.

The nature of the hydrogen atom, and thus the environment of the fourfold-coordinated phosphorus, can be inferred from the short T_2 (≤ 0.2 msec) of the phosphorus. The ^{31}P-^{1}H dipolar interaction will cause rapid decays of the echo in the spin-echo experiment *only if* the ^{1}H nucleus is coupled to other ^{1}H nuclei such that $\tau \geq T_{2,S}$. In a previous NMR study of ^{1}H in *a*-Si:H, it was reported that $T_{2,S} \approx 0.13$ msec for clustered hydrogen in *a*-Si:H.[21] This is sufficient to cause a rapid decay in the intensity of the echo of the fourfold-coordinated phosphorus. For example, for phosphorus bonded to a hydrogen atom which is coupled to the clustered hydrogen, Eqs. (4) and (6) predict that only $\sim 2\%$ of the ^{31}P echo would remain at $\tau = 0.25$ msec. The clustered hydrogen is also known to be associated with internal surfaces caused by defects in the structure.[21] Therefore, it is proposed that the fourfold-coordinated phosphorus sites are located at, or within ~ 5 Å of internal hydrogenated surfaces of *a*-Si:H.

The associated of fourfold-coordinated phosphorus sites with clustered hydrogen is consistent with a number of morphological and structural studies of doping in *a*-Si:H. Clustered hydrogen is known[10,21] to be associated with both columnar and noncolumnar microstructure, and such microstructure has been precipitated by the introduction of phosphorus into *a*-Si:H.[9] Furthermore, studies with nuclear profiling have shown[11,12] that the hydrogen content is higher in As- and B-doped layers of *a*-Si:H films than in intrinsic layers. In fact, an increase in the amount of clustered hydrogen has been observed by proton NMR when phosphorus is introduced.[10] Whether the hydrogen-rich surfaces act as "strain reliever" centers thereby accommodating a nearby fourfold-coordinated phosphorus atom, or the fourfold-coordinated phosphorus precipitates a hydrogen-rich surface, or some combination of these, requires a more detailed understanding of the chemical processes during the deposition of the films.

The distribution of sites (Table II) combined with the phosphorus content in each sample (Tables I and II), reveal further insights into the efficiency of phosphorus doping in *a*-Si:H. Assuming that the threefold-coordinated phosphorus sites yield energy levels deep in the valence band,[6] the increase in conductivity upon doping is due to the small fraction of fourfold-coordinated phosphorus. The NMR data show sample *A* has $\sim 1.7 \times 10^{20}$ cm^3 fourfold sites and sample *B* has $\sim 2.8 \times 10^{19}$ cm^3 fourfold sites and yet the samples have the same conductivity at room temperature. Clearly, the number of donor levels is not linearly dependent on the number of fourfold-coordinated phosphorus atoms. It appears that the doping efficiency of the fourfold-coordinated sites saturates at levels less than or equal to the content of sample *B*. The ineffectiveness of higher numbers of fourfold-coordinated sites may be related to the observation that the majority of the fourfold-coordinated phosphorus is at hydrogen-rich internal surfaces and/or autocompensation[13] of the donor levels.

Finally, we present the data of the compensated sample (sample *C* in Fig. 1 and Table II). Despite a decrease in conductivity of almost 4 orders of magnitude, the mole fraction of fourfold-coordinated sites has increased to about 67%. In addition, the spectrum of the fourfold-coordinated phosphorus has narrowed. One possible model to explain these data is the "activation" of fourfold-coordinated sites away from internal hydrogenated surfaces by the presence of boron acceptors. From a solid-state chemistry point of view this is not very appealing since it implies that changes in the electronic structure of *a*-Si:H (boron acceptor states) force new phosphorus bonds (P—Si or P—H). An alternative model, recently proposed to explain luminescence data,[13] involves the formation of phosphorus-boron complexes resulting in a donor-acceptor pair type of defect. The broadening on the fourfold-coordinated site is consistent with the ^{31}P-(^{10}B,^{11}B) heteronuclear dipolar interaction in a complex such as $(Si)_3P$-$B(Si)_3$. Furthermore, the center of mass is also consistent with studies of P-B complexes in solution.[26] Explicit B-P double-resonance experiments would be needed to confirm this suggestion; however, we find it a particularly appealing model in light of previous studies.[13]

IV. CONCLUSIONS

We report the first observation of ^{31}P NMR spectra in doped and compensated *a*-Si:H films. On the basis of chemical shifts, the spectra are interpreted in terms of threefold- and fourfold-coordinated phosphorus. In samples with 1.8 and 0.33 mol % phosphorus, the ratio of threefold- to fourfold-coordinated sites is approximately 4 to 1. From the ^{31}P-^{1}H dipolar couplings, it is proposed that the fourfold-coordinated phosphorus exists at hydrogen-rich internal surfaces. Significant changes in the ^{31}P line shape occurs when films are deposited with both diborane and phosphine, and we suggest these changes are due to formation of boron-phosphorus complexes within the film. These results have been discussed in relationship to the doping mechanism and other experimental observations in doped and compensated *a*-Si:H, and indicate that association of donor sites with known defect structures must be considered in amorphous semiconductors.

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