Donor States in Hydrogenated Amorphous Silicon and Germanium

M. Stutzmann and R. A. Street

Xerox Palo Alto Research Center, Palo Alto, California 94304

We report the first direct observation of phosphorus and arsenic donor states in hydrogenated amorphous silicon and germanium by electron-spin resonance. The states are identified via their characteristic hyperfine structure, and are attributed to neutral donors. A comparison with crystalline silicon and germanium shows that the disorder potential of the amorphous phase leads to a stronger localization and a wide distribution of donor states.

The investigation of shallow donors in crystalline silicon and germanium by magnetic resonance techniques since 1954 has led to a very detailed understanding of dopant states in these materials.[1-4] This is due to the capability of electron-spin resonance (ESR) and electron-nuclear double resonance (ENDOR) to map out the dopant wave function $\Psi_D(r)$ by the amount of hyperfine interaction between the doping electron and the magnetic moments of nuclei in the vicinity of the dopant atom. About ten years ago, the possibility to dope hydrogenated amorphous silicon (a-Si:H) with phosphorus and boron was discovered by Spear and Lecomber,[5] triggering the rapidly increasing use of amorphous silicon for a variety of applications. However, substitutional doping is closely linked to the topological constraints present in the solid phase and, therefore, the doping properties of crystalline and amorphous silicon can be expected to be quite different. So far, a better understanding of the doping mechanism in amorphous silicon has been limited by the lack of information about the electronic states and the detailed bonding configuration of the dopant atoms in the amorphous network.

As an example, consider the case of phosphorus doping. In crystalline silicon only fourfold coordinated sites, P_4, are formed. At sufficiently high temperatures, the donor electrons are thermally excited in the Si conduction band, leaving the donor atoms in the diamagnetic, ionized state, P_4^+. At lower temperatures the electrons remain localized at the donor atoms, which then are all in their neutral, paramagnetic charge state, P_4^0, and can be observed by ESR. In amorphous silicon, on the other hand, both threefold, P_3, and fourfold coordinated phosphorus, P_4, can be accommodated because the topological constraints of the crystalline lattice are relaxed. In fact, the current understanding of doping in this material is based on a chemical equilibrium between P_3 and P_4 states established during the plasma deposition of a-Si:H.[6] P_3 is the chemically preferred, lowest-energy configuration. It is, however, nondoping, since its electronic levels lie within the high density of states of the silicon valence band. Doping is only achieved by the relatively small fraction of phosphorus with fourfold coordination.

The incorporation of P_4 is promoted by the simultaneous formation of silicon dangling bonds. Then, most of the donor electrons become localized at deep dangling-bond states, which lowers the total energy necessary for P_4 incorporation and leaves most donors charged even at low temperatures.

This doping model can explain the experimental observation of a low doping efficiency and a doping-induced increase in the density of deep gap states in a semiquantitive way. However, there has not been a direct experimental observation of the donor or acceptor states in a-Si:H. In this paper, we present the first positive identification of such states in an amorphous semiconductor for the case of phosphorus and arsenic doping in a-Si:H and a-Ge:H. As in the corresponding crystalline semiconductors, the identification of the donor states is made possible by the characteristic hyperfine interaction between a localized donor electron and the dopant nucleus detected by ESR (X-band, 9.2 GHz). Samples were deposited under standard glow-discharge conditions using pure silane (SiH_4) or germane (GeH_4) with small volume fractions of phosphine (PH_3) or arsine (AsH_3) as dopant gases.

The hyperfine spectra observed at a temperature of 40 K in a-Si:H doped with phosphorus and arsenic are shown in Fig. 1. In both cases the well-known resonance of electrons localized in the Si conduction-band tail[7] appears near the free-electron position (dashed line), however, with considerably higher intensities for phosphorus than for arsenic doping. In addition to this central resonance, the ESR spectrum of phosporus-doped a-Si:H shows two lines of equal integrated intensity, split off from the free-electron position in an approximately symmetric way. This is indicative of a hyperfine interaction with a nucleus with spin $I = \frac{1}{2}$. (The offset of the two hyperfine lines in Fig. 1 from the zero signal level is due to overlap with the tails of the central resonance and the large-field modulation used.) A similar hyperfine structure is observed in phosphorus-doped a-Ge:H. In contrast, the arsenic-doped material exhibits four satellite resonances characteristic of hyperfine interaction with a nucleus of $I = \frac{3}{2}$. Obvious candidates for the nuclei in question are the isotopes ^{31}P and ^{75}As, both occurring with

100% natural abundance. Alternative hyperfine centers in phosphorus-doped samples, e.g., ^{13}C, ^{15}N, and ^{1}H, have been ruled out by preparing samples with similar doping levels under ultrahigh vacuum conditions and by isotope exchange of hydrogen with deuterium. In all cases the samples had identical hyperfine spectra. ^{29}Si can be excluded as a possible hyperfine center by the observation of a similar pair of hyperfine lines in phosphorus-doped a-Ge:H; germanium has no $I = \frac{1}{2}$ isotope.

The spectral position and the width of all observed hyperfine lines can be explained by the effective spin

Hamiltonian

$$H_{\text{eff}} = g\mu_B \mathbf{H} \cdot \mathbf{S} + A \mathbf{I} \cdot \mathbf{S}, \tag{1}$$

with an isotropic g value and isotropic hyperfine interaction A. Because of the stronger charge localization in the amorphous material, the interaction constant A in a-Si:H and a-Ge:H is significantly larger than in their crystalline counterparts, and second-order contributions to the energy levels in (1) have to be taken into account. These second-order terms are responsible for the asymmetric splitting and the different line shapes of the resonances in Fig. 1. The spectral positions of the $2I + 1$ hyperfine lines are obtained from Eq. (1) as

$$H(m_I) = H_0 - I(I+1)\Delta H^2/2H_0 - m_I \Delta H + (m_I \Delta H)^2/2H_0. \tag{2}$$

Here $H(m_I)$ are the magnetic field values at which spin resonance is observed, $H_0 = h\nu_0/g\mu_B$ ($\nu_0 =$ microwave frequency), M_I is the nuclear magnetic quantum number, and $\Delta H = A/g\mu_B$ is the field splitting between the $m_I = \pm\frac{1}{2}$ hyperfine lines. In order to reproduce the experimentally observed spectral width of the resonances, the anisotropy of the g value in amorphous silicon is not sufficient. Instead, a relative-

ly broad distribution of splitting constants is essential, which is easily understandable from the bonding disorder in the amorphous network. In Table I the mean values of ΔH and the full width at half maximum of the underlying distribution, W, are listed. Hyperfine splittings for the crystalline case are listed for comparison.

In Fig. 2, the dependence of the hyperfine splitting and the spin density on the phosphorus-doping level are shown for a-Si:H and a-Ge:H. The value for ΔH is independent of the doping level within the experimental accuracy (10 G). On the other hand, the intensity of both hyperfine lines increases roughly like the square root of the phosphorus concentration [solid lines in Fig. 2(b)], and is nearly two orders of magnitude larger in a-Si:H than in a-Ge:H. Also shown is the density of electrons occupying Si conduction-band-tail states (cb, central line of the ESR spectra), which saturates at high doping levels.

The hyperfine splitting clearly associates the new paramagnetic states with the phosphorus or arsenic atoms. Based on two further observations we argue that these states in fact must be the neutral-donor levels. First, the spin density of the hyperfine lines decreases strongly above a temperature of 200 K. This demonstrates that the states must have an energy level
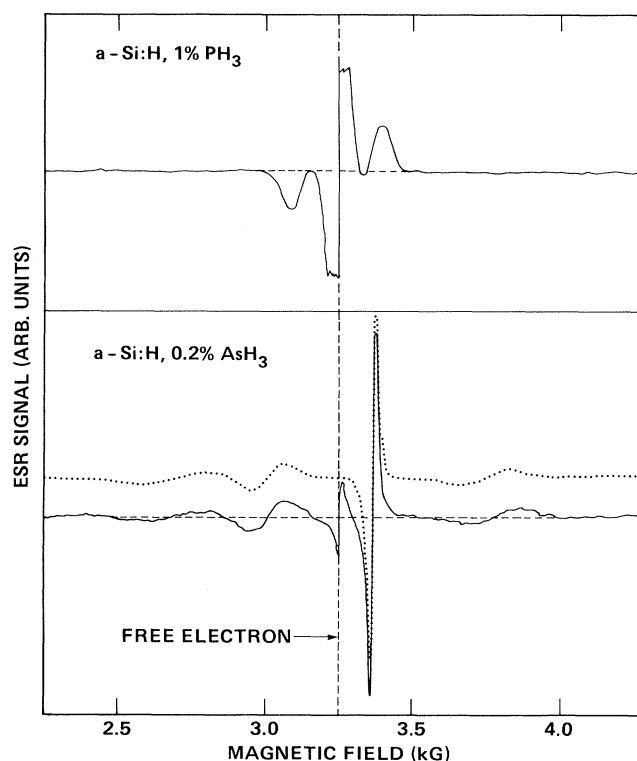

FIG. 1. ESR spectra of donor states in phosphorus- and arsenic-doped hydrogenated amorphous silicon. The dotted line shows the theoretical hyperfine spectrum for arsenic-doped a-Si:H calculated from Eq. (2) with the fitting parameters given in Table I.

TABLE I. Hyperfine splitting constants ΔH in crystalline and amorphous silicon and germanium doped with phosphorus or arsenic. In the amorphous phase ΔH is an average value for a distribution with full width at half maximum W. All values are given in gauss.

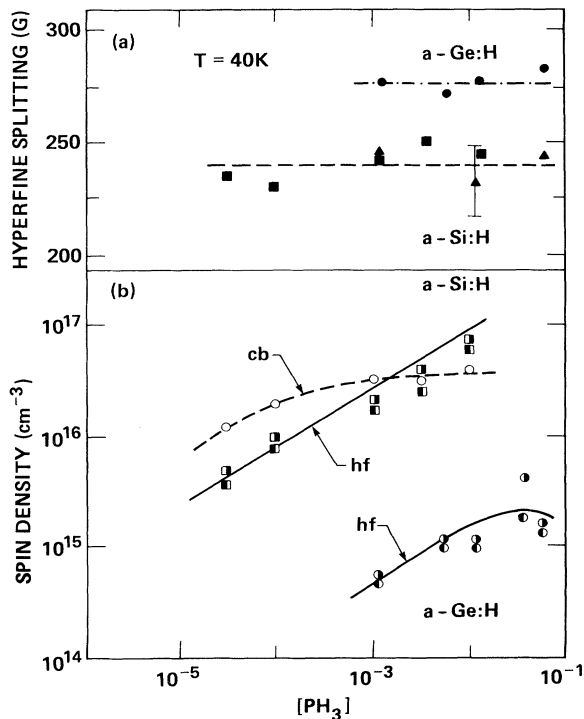| Host	Donor	ΔH(cryst.)	ΔH(amorph.)	W
Si	P	42	245	165
Si	As	71	355	150
Ge	P	21	275	70
Ge	As	36	$\cdots$	$\cdots$

FIG. 2. Dependence of (a) the hyperfine splitting ΔH and (b) the ESR spin density on the gas-phase phosphorus doping level in a-Si:H and a-Ge:H. Left- and right-shaded symbols in (b) refer to the $m_I = \frac{1}{2}$ and $m_I = -\frac{1}{2}$ hyperfine lines, respectively. The dashed line (cb) shows the density of electrons in Si conduction-band-tail states.

FIG. 3. Density of occupied shallow states in phosphorus-doped a-Si:H determined by ESR and transient-voltage experiments as a function of the doping level. cb and hf refer to electrons in tail states and in hyperfine split states, respectively.

close to the Fermi energy, which for dopant concentrations larger than 10^{-5} is 150–200 meV below the conduction-band mobility edge for the phosphorus-doped samples. For the arsenic-doped material the corresponding energy is slightly larger, 200–250 meV. By analogy with crystalline silicon, we interpret the temperature dependence as thermal ionization of the donor electrons into delocalized states. The ionization temperature is higher than in crystalline silicon because the donor levels are deeper.

The second point concerns the spin density which is again shown in Fig. 3. However, now the densities of the hyperfine split states and of the tail states have been added (cb+hf) to give the total density of paramagnetic states near the Fermi energy. The density of electrons in shallow states lying within a few kT of the Fermi energy in doped a-Si:H has also been measured indepedently by transient-voltage techniques.[8] Here a short voltage pulse is used to sweep out all charges in a sample that can respond to this pulse on the time scale of the experiment. For sufficiently short pulses the sweep out of electrons in deep states is negligible because of their small thermal emission rates. Thus, the charge collected in such a
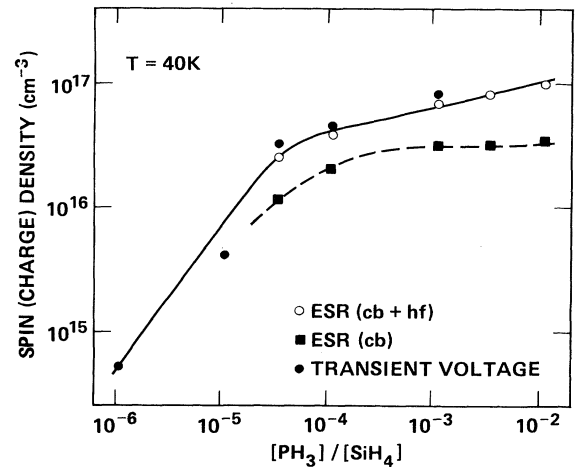
transient-voltage experiment is a direct measure for the density of shallow states near the Fermi level. The results in Fig. 3 show that the charge density measured in this way agrees with the ESR data within the experimental uncertainty of a factor of 2. The same agreement is observed for the arsenic-doped samples. This provides conclusive evidence for the quantitative correspondence between the hyperfine-split spin states observed in ESR and the shallow electronic states seen in the sweep-out experiments.

Hence, a consistent model emerges in which the donor levels form a relatively broad distribution of states in the same energy range as the Si-Si weak antibonding states constituting the conduction-band tail in amorphous silicon. Most of these donor states are empty even at low temperatures, owing to the possible charge transfer of donor electrons into the deep-lying, doping-induced dangling bonds. If, however, the density of compensating dangling bonds is smaller than the density of fourfold-coordinated donor sites, P_4, the Fermi energy can intersect the lower part of the donor distribution. Donor states below the Fermi energy will then be neutral and can be observed by ESR. It is important to emphasize that the fraction of neutral donors is very small. At a doping level of 10^{-3}, the sample contains approximately 10^{20} cm^{-3} phosphorus atoms. Of these, about 10^{18} cm^{-3} are fourfold coordinated, and only 10% of these are neutral and observed in ESR.[6]

Some final comments can be made concerning the donor states. The larger hyperfine interaction compared to the crystalline case, and the existence of a broad distribution of states with similar electronic character is a natural consequence of the disorder-

induced localization in amorphous semiconductors. For s-like electronic states, the hyperfine interaction is mainly determined by the overlap of the donor wave function with the nucleus,[9] $\Delta H \propto |\Psi_D(0)|^2$. In this case, ΔH should increase with increasing localization of the wave function. Assuming a similar envelope shape and an equal influence of central-cell corrections for the crystalline and amorphous donor wave functions, we obtain a phosphorus donor radius in a-Si:H and a-Ge:H of about 10 Å. For arsenic, the radius is slightly smaller, ≈ 9 Å, as is to be expected from the larger ionization energy for this donor. These values are significantly smaller than in crystalline material,[2,4] and are in good agreement with previous estimates using luminescence data.[10] Second, the missing long-range order in the amorphous material causes a broadening of the sharp crystalline donor levels. This gives rise to the distribution of splitting constants listed in Table I. Finally, the larger density of hyperfine states compared to the density of unsplit band-tail states obtained for arsenic doping (cf. Fig. 1) suggests that As forms deeper donor states in a-Si:H than P, as it is the case in crystalline silicon.

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