Dopant states in a-Si:H. III. Triply coordinated boron

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Boron atoms at trigonal, alloying sites are shown to be electronically active in a-Si:H. Alone among the dopant elements of groups III and V, boron produces deep gap states in this configuration. The position of a level depends on the bond angle of the site and thereby its occupation. We predict that there will be a conduction tail of empty levels and a long valence tail due to paramagnetic B_3^- sites. We discuss evidence that such states have been seen in luminescence, optical-absorption, and transport experiments.

I. INTRODUCTION

It is generally believed that dopants of groups III and V can occupy two types of site in a-Si:H, a "substitutional" fourfold (or $\langle 4 \rangle$) electronically active site, and a more common threefold or ($\langle 3 \rangle$) "alloying" site. Impurities at alloying sites are assumed to be passive because the atom is able to satisfy its normal valence requirements, and so these sites merely reduce the doping efficiency. We show that all group-V elements and most group-III elements are indeed passive, but triply coordinated boron B_3 produces deep gap states in a-Si:H. We find a strong occupation dependence of the energy levels due to relaxation, making them efficient nonradiative recombination centers.

The origin of boron's gap states is easily seen from a table of orbital energies, such as Table I. A symmetric $\langle 4 \rangle$ site possesses sp^3 hybrids at energy $\frac{1}{4}\epsilon_s + \frac{3}{4}\epsilon_p$. If each hybrid forms a bond, then bonding (σ) and antibonding (σ^*) states are formed on either side of the hybrid energy. If such a sp^3 site has only three neighbors, the unbonded hybrid, or dangling bond, remains at the hybrid energy and gives a gap state, as in a-Si. Group-III and -V elements are naturally trivalent and do not give gap states because they adopt different bond angles. Group-V elements are s^2p^3, form p bonds with angles close to 90°, leaving a nearly s-like nonbonding level deep in their valence bands. Group-III elements may bond in planar $\langle 3 \rangle$ sites using sp^2 hybrids leaving an unoccupied nonbonding $p\pi$ orbital. This level is assumed to lie well into the conduction band of a-Si, giving a passive site. Table I shows that the p energies of all group-III elements except boron lie well above the sp^3 energy of Si. In contrast, boron has a p energy only 0.9 eV higher and thus may lie in the upper gap of a-Si. Worse, if the boron site distorts, the nonbonding state acquires some s character and drops in energy. The boron sp^3 energy lies 0.3 eV below that of Si. Thus boron may produce levels in any part of the gap of a-Si.

These simple bonding pictures are confirmed by detailed cluster calculations in the next section. The pyramidal angle of B_3 depends on the occupancy of the nonbonding orbital and the constraints imposed by the rest of the network. We show in Sec. III that the gap level energy depends strongly on ϵ_F and thereby on doping and compensation. Boron is known to be a more problematic dopant than P or As. In Sec. IV we discuss evidence from luminescence, optical, and transport data that B-centered deep levels could be one of the causes.

II. CLUSTER CALCULATIONS

The electronic structure of various trivalent impurities has been calculated using a semiempirical tight-binding (TB) Hamiltonian and the recursion method. The TB Hamiltonian uses a sp^3s^* basis

TABLE I. Hartree-Fock s- and p-orbital energies in eV [from W. A. Harrison, Phys. Rev. B 24, 5835 (1981)].

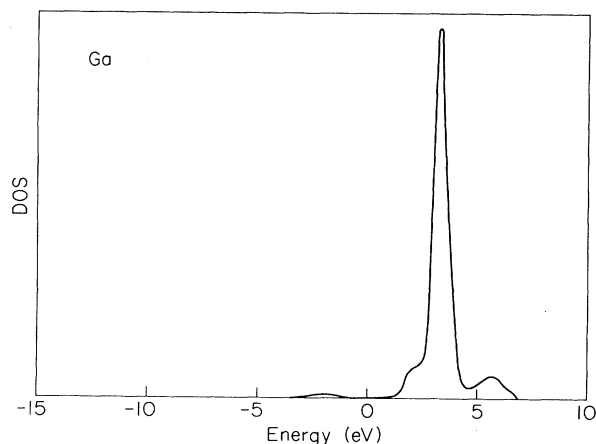|	Si	B	Al	Ga	In	Tl	N	P	As	Sb
$-E(s)$	14.79	13.46	10.70	11.55	10.14	9.82	26.22	19.22	18.91	16.02
$-E(p)$	7.58	8.43	5.71	5.67	5.37	5.23	13.84	9.54	8.98	8.14
$-E(sp^3)$	9.38	9.69	6.96	7.14	6.56					

FIG. 1. LDOS for the $p\pi$ orbital at a planar $\langle 3 \rangle$ Ga site, referred to the valence maximum of c-Si.

and retains only first-neighbor interactions, as described in more detail earlier.[1,2] All the energies are referenced to the valence maximum of crystalline (c-) Si for convenience. The recursion method represents the Hamiltonian of the cluster as a continued fraction, truncated after a number of levels, which is then manipulated to give the local densities of states (LDOS) on the selected atom.[3] Thirty-five levels of the fraction are retained in the present calculation. The positions and orbital content of the gap states is found from the poles of the Green's function.[4]

The cluster consists of three separate crystalline units of 128 Si atoms connected only via the impurity atom at the vertex, whose angle is allowed to vary. A planar vertex has D_{3h} symmetry in which
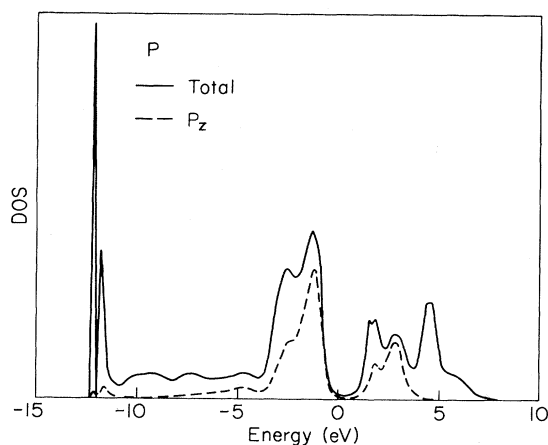
only the $p\pi$ orbital is A'_1. A pyramidal site is C_{3v} in which both p_z and s belong to A_1 and may hybridize. The LDOS for all four s and p orbitals or just the p_z obital can be displayed; usually the latter is more informative.

The LDOS of the $p\pi$ orbital at a planar Ga site is strongly concentrated around 3.3 eV, the p-orbital energy, showing its nonbonding character (Fig. 1). Similar results are found for Al and In. If the vertex angle is decreased to give bond angles of 109.5°, the nonbonding level falls but always remains above 2 eV for these elements. Together, the results confirm the passivity of $\langle 3 \rangle$ Al, Ga, and In sites.

Figure 2 shows the LDOS for a $\langle 3 \rangle$ P site with its usual 98° bond angle. There are no gap states. The nonbonding orbital is the s-like resonance seen at the bottom of the valence band. The p_z orbital is involved in the σ and σ^* states around -2 and 3 eV. Similar results are found for the other pnictides, also confirming that their $\langle 3 \rangle$ configurations do not produce gap states.[5]

Figure 3 shows the LDOS of the B p_z orbital at $\langle 3 \rangle$ sites with bond angles of 120° and 109.5°. Both configurations produce gap states at 1.0 and 0.05 eV, respectively.[4] These energies are within 0.1 eV of the p and sp^3 energies, confirming that the bond angles determine the hybridizations.[6] The B $p\pi$ level is expected to be insensitive to its environment like the occupied $p\pi$ levels in Se. The dangling bond energy varies with its environment, and Fig. 3 shows that this will be largely through the effects of bond-angle variations on its hybridization. Hence $\langle 3 \rangle$ boron is not electronically passive. The difference in behavior between B and the other group-III elements is caused by its lower p energy and its relatively small s-p energy difference.

FIG. 2. LDOS of the four sp^3 orbitals and of the A_1 p_z orbital at a $\langle 3 \rangle$ P site with 98° bond angles.
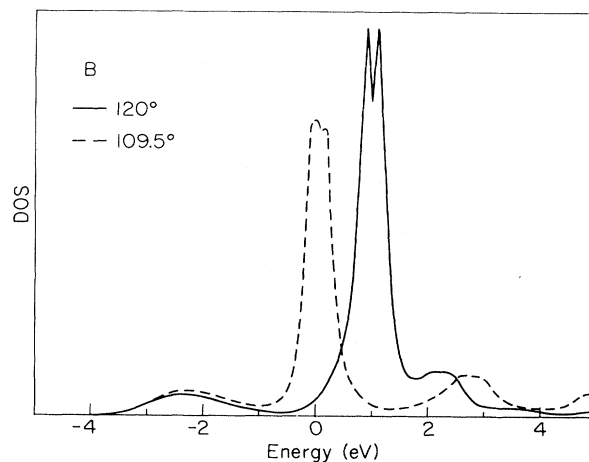

FIG. 3. LDOS for the p_z orbital at a $\langle 3 \rangle$ B site with 120° and 109.5° bond angles.

III. POSITION OF THE GAP STATES

We have shown the dangling-bond energy of $\langle 3 \rangle$ B to depend on its bond angle. In the "molecular limit" in which both the on-site correlation energy and the constraints imposed by the rest of the network are neglected, the angle varies to optimize the hybridization for each occupation number, as in a $X\mathrm{H}_3$ molecule. In this limit, B_3^0 is planar, B_3^- has angles of 109.5^0, and B_3^{2-} would have angles close to $90°$. Additionally, the diamagnetic B_3^0 and B_3^{2-} states would be more stable and the reaction

$$2\mathrm{B}_3^- \rightarrow \mathrm{B}_3^0 + \mathrm{B}_3^{2-}$$
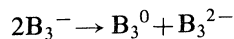
would be exothermic, implying that B_3 possessed a negative effective correlation energy or "negative U."[7-9] We argue that the molecular limit does not hold for B_3 sites. Similar bonding configurations have been suggested for Si atoms in buckling models of the 2×1 reconstruction of the (111)Si surface[10] and for dangling bonds in a-Si.[11] These forms of surface reconstruction have recently been shown to be less stable than the undistorted surface,[12] and the Si dangling bond is now known to have a positive U.[13] We believe the correlation energy of B_3 to be much larger than for Si_3 because of boron's smaller radius and particularly because of the low stability of a highly charged B^{2-} gap state on an electropositive element.[14] We propose that B_3^0 and B_3^- to be the observable gap states of $\langle 3 \rangle$ B, and that each will have metastable distorted configurations.

We position B_3 levels in the gap of a-Si:H using the energies in Fig. 3 as a guide. The gap of a-Si:H is about 1.6 to 2.0 eV wide.[15-17] Taking a value of 1.8 eV, we argued earlier[1] that the edges should be placed at -0.5 and 1.3 eV with respect to the valence maximum of c-Si, the reference energy of our calculations. Deep-level transient spectroscopy (DLTS) places the D^- Si dangling-bond state 0.8 eV below E_c,[17] 1.0 eV above E_v (Fig. 4). Its correlation energy is 0.4 eV,[16,18-20] placing D^0 0.6 eV above E_v, 0.1 eV above E_v in c-Si. Our calculations place the Si_3 level at 0.24 eV in c-Si, 0.14 eV higher than this. By subtracting this figure from all our calculated levels, the planar and tetrahedral B_3 sites lie at about 1.4 and 0.4 eV above E_v in a-Si:H, respectively. Scaling the Si correlation energy to the smaller radius and valence of B, we estimate it to be at 0.6 eV, placing the B_3^{2-} planar state well above E_c, where it would delocalize into the extended conduction states. A much larger correlation energy of 1.4 eV is needed to force the tetrahedral B_3^{2-} site above E_c also, but this is probably necessary. In summary, B_3 has three charge states: B_3^0 which prefers to be planar, B_3^- which prefers bond angles of $109.5°$, and
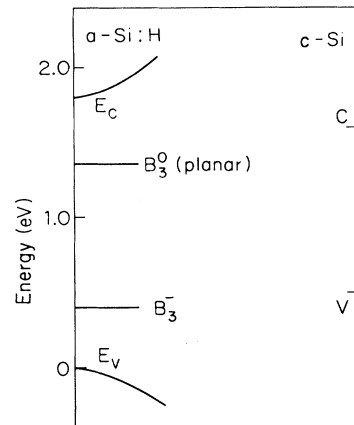

FIG. 4. Predicted energy levels for $\langle 3 \rangle$ B sites in a-Si:H, with the valence maximum of c-Si assumed to lie at $+0.5$ eV.

B_3^{2-} lying above E_c. The lower charge states are both accessible by varying the doping polarity. A boron ESR signal from B_3^- should be seen in compensated samples.

IV. DISCUSSION

Gap states due to boron dangling bonds should be most evident in compensated samples. With unipolar doping, ϵ_F lies close to the valence-bond edge E_v and the B_3 sites preferentially adopt their planar configuration giving states close to E_c, far away from ϵ_F. Compensation raises ϵ_F above the B_3^- level causing more borons to distort and produce states away from the band edges. We discuss evidence that boron centers have been seen in luminescence, transport, and optical measurements.[20-22]

Gap states in doped a-Si:H can be both Si dangling bonds and extrinsic dopant centers. Unfortunately, the density of Si dangling bonds depends on the doping level so their effects in doped films cannot be just subtracted away. It is found that the luminescence efficiency of a-Si:H decreases with doping level due to an increased density of recombination centers, attributed to Si dangling bonds.[23] Compensation reduces the number of Si dangling bonds, but Dersch et al.[19] found that their number increases above the undoped level if ϵ_F is held near midgap. Behind all these variations in dangling-bond density, Street et al.[21] note that the 1.4-eV luminescence peak shifted to lower energies with increased doping in compensated samples. This was assigned to the growth of a large tail of states out of the valence band. The tail causes the red shift in the luminescence peak and is only found in the compensated samples. In uncompensated samples the peak

remains at a fixed energy but reduces in intensity with heavier doping. As the tail is only found in compensated samples, it is tentatively identified with the dangling-bond levels of the 109.5° B site in Fig. 4. As they are singly occupied, they should be identifiable by their ESR signal. The tail should also be absent in compensated Ga-doped a-Si:H.

The transport mechanism in doped a-Si:H films can be analyzed from combined conductivity and thermopower measurements. Boron doping is found to affect electron transport as well as providing free holes.[22] In uncompensated samples, planar B_3 levels are expected to introduce a 0.4-eV tail below E_c, which would modify electron mobilities. There is some evidence of a valence tail in p-type samples from the difficulty of DLTS measurements. This may indicate that B could adopt a pyramidal site in p-type samples which would require $B_3^- \text{-} D^+$ complexes. Any tail does not itself prevent doping, some of the lowest conductivity activation energies have been found in p-type chemical-vapor-deposition (CVD) a-Si films.[24]

Band tailing can also be identified by optical absorption. It has been observed in both P- and B-doped samples.[20] In the P-doped samples, n-type photoconductivity was found when the tail states were excited proving them to be valence tail states, interpreted as Si dangling bonds. The tailing band has yet to be positively identified in the B-doped samples. However, the experimental absorption spectrum is consistent with our model of B π states just below E_c. This could be confirmed if a light-induced ESR signal due to B was observed for a 1.2-eV excitation.

Nuclear magnetic resonance and Raman spectroscopy should both be able to test the model. The NMR linewidth of B is too large to be ascribed to $\langle 4 \rangle$ sites and is known to decrease as the site becomes more pyramidal.[25] NMR should find a narrower B line in compensated samples or samples in which an electric field during deposition causes the occupation of the p_z state. The A_1 vibration of B along the z axis is polarized and only Raman active if the site is pyramidal. Its frequency increases from a low value as the site distorts.

Al, Ga, and In should be simpler p-type dopants

because their $\langle 3 \rangle$ sites are passive. However, the levels of their $\langle 4 \rangle$ sites are not as shallow as boron's.[1] Trivalent Al, Ga, and In compounds are strong Lewis acids with a great tendency to over-coordinate, as in Al_2Cl_6. This will obviously increase doping efficiencies. A possible problem is that the low stability of $\langle 3 \rangle$ sites may manifest itself instead as autocompensation by the formation of $Ga^{3+}(Ga_3^-)_3$ complexes.

V. CONCLUSIONS

Our model can be summarized as follows. Triply coordinated boron produces deep gap states in a-Si:H, at positions very close to those expected from its orbital energies. As yet there is no direct ESR evidence of deep boron levels in a-Si:H, but the simplicity of the energy arguments suggests that boron's dangling-bond states must be deep and we give indirect evidence that such centers have been seen. In p-type samples planar sites are expected to cause a 0.4-eV-wide conduction tail which could be identified by subgap optical absorption and light-induced ESR (LESR). Compensation transforms the conduction tail into a valence tail of singly occupied states due to pyramidal B_3 sites. Their levels should be singly occupied giving a cold dark ESR signal and subgap absorption. We suggest that NMR and Raman spectroscopy on variably compensated samples could prove the model. We also suggest that the strong electron-lattice coupling associated with these sites will make them efficient nonradiative centers. In this respect they may be much more deleterious than silicon dangling bonds as their levels span the whole gap between both band tails. We also predict that Al, Ga, and In should be chemically simpler p-type dopants because their $\langle 3 \rangle$ sites are passive. The difference between B and the other acceptors is due to its lower p energy and smaller s-p splitting.

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[1]J. Robertson, this issue, Phys. Rev. B 28, 4647 (1983); B 28, 4658 (1983).
[2]P. Vogl, H. J. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids (in press).
[3]R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C 5,

2845 (1972); 8, 2591 (1975); in Solid State Physics, edited by H. Ehrenreich, D. Turnbull, and F. Seitz (Academic, New York, 1980), Vol. 35, p. 216.
[4]The Green's function is real in a gap and it can be obtained from the recursion method and expressed as a series of poles at E_i, one for each level of the continued

fraction:

$$G(E) = \sum_i w_i (E - E_i)^{-1} .$$

Poles lying in the gap correspond to gap states whose orbital character is given by w_i (Ref. 1).

[5]Planar P sites also give gap levels but this configuration is energetically very unfavorable.

[6]Hybridization does not always follow the bond angle directly once tetrahedral symmetry is lost; see, for example, Se [J. Robertson, Philos. Mag. 34, 13 (1976)].

[7]N. F. Mott, J. Phys. C 13, 5433 (1980); R. A. Street and N. F. Mott, Phys. Rev. Lett. 35, 1293 (1975).

[8]M. Kastner, H. Fritzsche, and D. Adler, Phys. Rev. Lett. 37, 1504 (1976); M. Kastner and H. Fritzsche, Philos. Mag. B 37, 199 (1978).

[9]J. Robertson, Phys. Chem. Glasses 23, 1 (1982).

[10]D. Haneman, Phys. Rev. 121, 1093 (1961); W. A. Harrison, Surf. Sci. 55, 1 (1976).

[11]S. R. Elliott, Philos. Mag. B 38, 325 (1978); D. C. Allan and J. D. Joannopoulos, Phys. Rev. Lett. 44, 43 (1980).

[12]K. C. Pandey, Phys. Rev. Lett. 49, 223 (1982), 47, 1913 (1981).

[13]R. A. Street and D. K. Biegelsen, Solid State Commun. 33, 1159 (1980).

[14]Negative U boron centers are observed in c-Si, but these have a very different split-interstitial configuration with lower charge states; B^+, B^0, and B^- without the less stable B^{2-} [R. D. Harris, J. L. Newton, and G. D. Watkins, Phys. Rev. Lett. 48, 1271 (1982)].

[15]G. D. Cody, T. Tiedje, B. Abeles, B. Brooks, and Y. Goldstein, Phys. Rev. Lett. 47, 1480 (1981).

[16]H. Overhof and W. Beyer, Phys. Status Solidi B 107, 207 (1981).

[17]D. V. Lang, J. D. Cohen, and J. P. Harbison, Phys. Rev. B 25, 5285 (1982); J. D. Cohen, D. V. Lang, and J. P. Harbison, Phys. Rev. Lett. 45, 197 (1980).

[18]J. D. Cohen, J. P. Harbison, and K. W. Wecht, Phys. Rev. Lett. 48, 109 (1982).

[19]H. Dersch, J. Stuke, and J. Beichler, Phys. Status Solidi B 105, 265 (1981); 107, 307 (1981).

[20]W. B. Jackson and N. M. Amer, Phys. Rev. B 25, 5559 (1982); W. B. Jackson, Solid State Commun. 44, 477 (1982).

[21]R. A. Street, D. L. Biegelsen, and J. C. Knights, Phys. Rev. B 24, 969 (1981).

[22]W. Beyer and H. Mell, Solid State Commun. 38, 216 (1981).

[23]R. A. Street, D. K. Biegelsen, and J. C. Knights, Phys. Rev. B 18, 1880 (1978); R. A. Street ibid. 21, 5775 (1980); Adv. Phys. 30, 593 (1981).

[24]J. Margarino, D. Kaplan, A. Friedrich, and A. DeNeufville, Philos, Mag. B 45, 285 (1982).

[25]S. G. Greenbaum, W. E. Carlos, and P. C. Taylor, Solid State Commun. 43, 663 (1982).