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Dopant states in *a*-Si:H. II. Effects of H and F

John Robertson*
Department of Physics, University of Illinois, Urbana, Illinois 61801
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The electronic structures of a variety of Si-H, Si-F, dopant-H, and dopant-F configurations have been calculated with the use of the tight-binding method. Monohydrogenated dopant sites are found to give levels no deeper than their parent sites with four Si neighbors, in general, while fluorinated donor levels are slightly deeper. We suggest that the size of an observed field-induced doping effect cannot be explained by changes in dopant levels with hydrogen attachment, and prefer an explanation based on Fermi-level—dependent dopant coordinations. New tight-binding parameters are presented for the Si—H bond using only first-neighbor interactions but including the H $2p$ state. This gives more easily transferable parameters for the amorphous state, which also represent the polarized H-charge distribution in the Si—H bond. With these parameters we find that monohydride units, including the idealized hydrogenated vacancy, do not give gap states but that the conduction band of polysilane $(SiH_2)_n$ extends down to 0.3 eV. We show that the valence band of *a*-Si:H retreats by a maximum of $V(pp\pi)$ if only monohydride units are present.

I. INTRODUCTION

The hydrogen content of *a*-Si:H is sufficiently large that hydrogenated dopant sites must be considered separately as possible sources of deep gap states. The presence of hydrogen also appears to be intimately linked to the detailed microstructure of *a*-Si:H. This paper, which is paper II of the series, extends our calculations on dopant states in *a*-Si (Ref. 1) to consider various dopant configurations involving H and F. We show that, in general, monohydride and monofluoride substitutional fourfold (or $\langle 4 \rangle$) sites still give levels that are as shallow as those sites surrounded by four silicons.

The passivating effect of H and F is crucial to obtaining useful doping in *a*-Si.[2] Silicon dangling bonds produce a high density of gap states in evaporated or sputtered *a*-Si which are converted by hydrogen into bonding (σ) and antibonding (σ^*) Si-H states, lying in the bands. As a preliminary to studying the dopant states, the electronic structure of various configurations of H and F is calculated: the hydrogenated vacancy, *cis* and *trans* Si—H bonds, the $(SiH_2)_n$ polymer, together with some of their fluorine counterparts. This necessitates choosing tight-binding (TB) parameters for the Si—H and Si—F bonds. Our TB calculations in paper I employed a Hamiltonian restricted to first-neighbor interactions but with an extended sp^3s^* basis. We parametrize the Si-H interactions here in a similar spirit using an extended sp^* basis for H.

The hydrogen content of *a*-Si:H is much greater than needed to passivate only the Si dangling bonds.[2] It is attributed to the replacement of weak reconstructed Si—Si bonds by Si—H bonds at incipient and internal surfaces in *a*-Si. This causes an inhomogeneous hydrogen distribution, confirmed by NMR as a clustering of monohydride groups $\equiv$Si—H.[3,4] Hydrogen contents over 5% can be produced by varying the deposition conditions. Lower temperatures or faster growth rates lead to a two-phase structure, seen by electron microscopy, consisting of columnar regions of high density, low-H content *a*-Si together with "connective tissue" containing more H in the form of $=SiH_2$ groups.[5–9]

The clustering of hydrogen may also cause an inhomogeneous distribution of dopants with shallow levels. There has been interest recently in microcrystalline Si, in which doping is more effective in the small crystalline regions.[10] Naturally, by analogy one might question the effectiveness of monohydride dopant centers at internal surfaces. Additionally, it has been suggested that threefold (or $\langle 3 \rangle$) pnictide sites segregate towards surfacelike regions and that $\langle 3 \rangle$ sites of group-III atoms segregate towards the interior,[11] which could enhance any such effect.

Fluorine is also a good passivant in *a*-Si because the Si—F bond is stronger than the Si—H bond. Early interest focused on reports that *a*-Si:(F,H) had a lower gap-state density and higher attainable conductivities than *a*-Si:H,[12] but recent deep-level transient spectroscopy measurements find less difference.[13] Thus we also study fluorinated sites.

Passivant processes may also be involved in a range of metastable effects in *a*-Si.[14–16] Staebler

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and Wronski discovered a photoinduced reduction in the dark and photoconductivity.[14] Although this effect is still the matter of some debate,[17–20] it appears to be related to changes in the bulk density of gap states.[21] The size of the effect appears to depend on the deposition conditions of the film and seems to be less in homogeneous chemical-vapor-deposited (HOMOCVD) a-Si:H and some a-Si:F materials.[22] Imperfect passivation and hydrogen mobility are two of a number of suggested mechanisms for this effect and may be related to whether neighboring H and F atoms can convert a shallow center into a deep center.

II. Si-H STATES

We calculated the electronic structure of the four Si-H configurations shown in Fig. 1: the hydrogenated vacancy (HV), a hexagonal layer of SiH having *trans* Si—H bonds, an orthorhombic SiH structure possessing *cis* Si—H bonds, and the $(SiH_2)_n$ polymer "polysilane." Generally, our results support those of previous workers[23–30] and are in line with experiment.[31,32]

The hydrogenated vacancy is a useful theoretical construct in which the four dangling bonds directed into a vacancy have each been saturated by a hydrogen atom. It preserves the original T_d symmetry and so can be treated as a substitutional impurity by defining effective s and p orbitals from A_1 and T_2 combinations of the four H s orbitals, as in the Appendix. We find this "impurity" produces no states between -0.7 and 1.4 eV in c-Si. The local H density of states (DOS) was calculated using the recursion method[33] (Fig. 2). The valence-band DOS has a broad peak from -4 to -7 eV and a lower peak at -11 eV. The conduction DOS is also broadly peaked around 3 eV. Our local DOS is in better agreement with the pseudopotential results[23] than

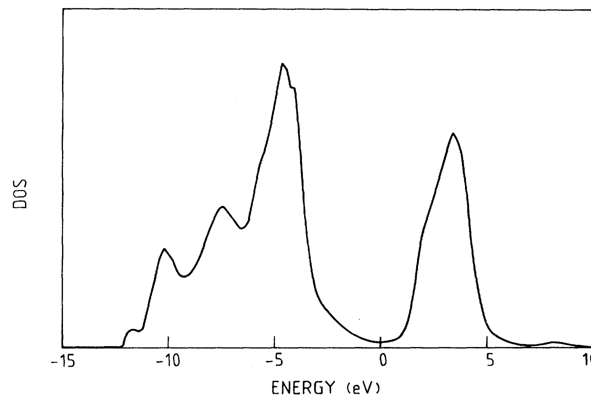

FIG. 2. Partial H DOS for the hydrogenated vacancy.

both previous TB results.[27,28]

Two advantages are apparent from using only first-neighbor Si-H and Si-Si interactions for the HV. Firstly, the second-neighbor parameters of Pandey produce gap states[27] unlike the other calculations. Secondly, the DOS of Fig. 2 is more likely to represent that of an isolated $\equiv$Si—H unit because of the better transferability of first-neighbor parameters.

The bands and DOS for hexagonal SiH in Fig. 3 and the orthorhombic SiH layer in Fig. 4 illustrate most of the features expected for Si—H bonds. Hexagonal SiH has D_{3d} symmetry and can be visualized as a single $\langle 111 \rangle$ layer of Si hydrogenated on both sides. The valence-band maximum of hexagonal SiH has retreated to -0.72 eV and is of pure $SiP_{x,y}$ character. Its conduction-band minimum lies at 1.04 eV and is formed from Si-H σ^* states. The valence-band DOS possesses H-like peaks at -5 and -7 eV, identified as signatures of the underlying hexagonal Si rings.[28] The orthorhombic structure also has a valence maximum at -0.72 eV, but has a

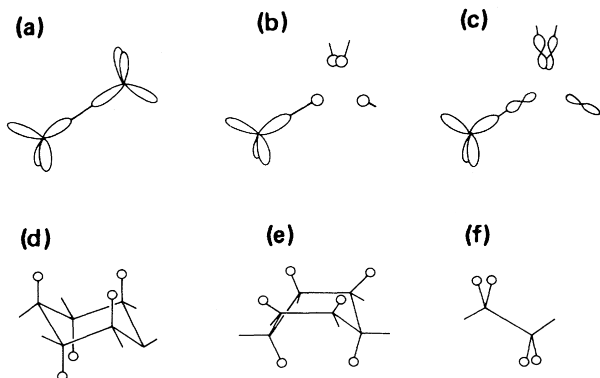

FIG. 1. Atomic configurations in a-Si: (a) orbitals on nearest-neighbor sites, (b) hydrogenated vacancy, (c) fluorinated vacancy, (d) hexagonal SiH, (e) orthorhombic SiH, and (f) polysilane, $(SiH_2)_n$.

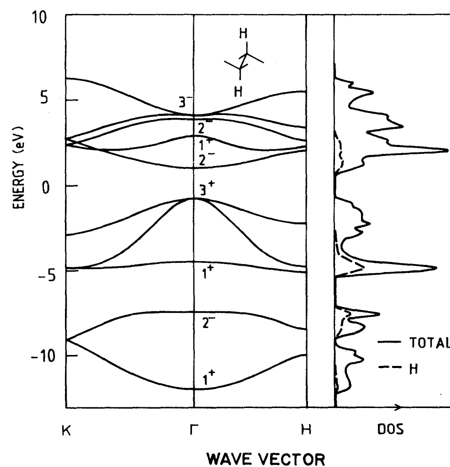

FIG. 3. Bands and DOS for hexagonal SiH.

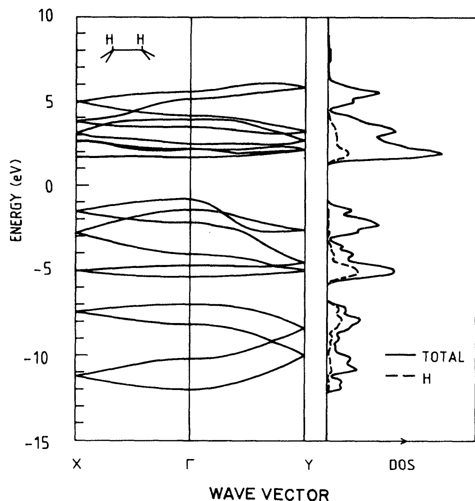

FIG. 4. Bands and DOS for orthorhombic SiH.

much higher conduction-band minimum at 1.7 eV which is also Si-H σ^*-like. Its valence band has peaks at -5 and -7 eV, but the lower one is broader.

The cause of the erosion of the upper valence band and changes in the character of the conduction edge are easily seen in these idealized configurations. The valence maximum of c-Si is formed from all three p orbitals and lies at

$$E(p)-\tfrac{4}{3}[2V(pp\pi)+V(pp\sigma)] .$$

Only the $p_{x,y}$ orbitals are involved in the valence maximum in both layer structures and it now lies at

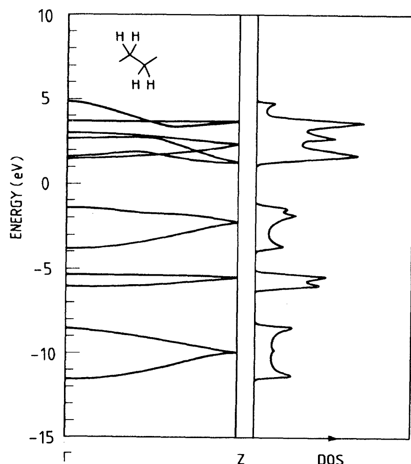

FIG. 5. Bands and DOS for polysilane.

$$E(p)-[5V(pp\pi)+4V(pp\sigma)]/3 ,$$

with the p_z orbital forming the deeper Si-H states. Thus we suggest that the maximum erosion of the valence band is $V(pp\pi)$ in a-Si:H (or a-Si:F) containing only monohydride groups. Joannopoulos noted that fluctuations in the valence edge between H-rich and H-free regions may cause the lower hole mobility.[27] Our results show that the conduction-band minimum could also be subject to fluctuations if any adjacent monohydride groups adopt *cis* positions. Assuming equal proportions of *cis* and *trans* units in highly hydrogenated a-Si:H, we estimate that a maximum mean gap of 2.1 eV for a-Si:H (and 2.4 eV for a-Si:F).

The bands and DOS of polysilane in Fig. 5 show a gap from 1.4 to 1.3 eV. Thus, our results suggest that $(SiH_2)_n$ chains do not give gap states, contrary to Ching *et al.*[29] The upper valence band is Si σ p_z—like with z along the chain axis, and the low conduction bands are Si-H σ and Si-Si σ^*.

A number of comments on the electronic structure of inhomogeneous a-Si:H can be made, based on these results. Although the hydrogenated vacancy is a theoretical construct, related hydrogen groupings are found in random network models of a-Si:H because of the difficulty of closing the Si network around a single Si—H unit.[34] Monohydride units could form little clusters resembling distorted, dilated hydrogenated vacancies and possess local DOS such as in Fig. 2. The NMR linewidth of an "idealized" hydrogenated vacancy of crystalline dimensions is much larger than observed experimentally.[3] The strongest clustering consistent with NMR data is roughly three hydrogens in a volume the size of a crystalline trivacancy. Hydrogens in such configurations would still possess a similar local H DOS, being dominated by Si-H not H-H interactions. Phillips[11] suggested that internal surfaces in a-Si possess a $\langle 111\rangle$-like topology so that layers of *trans* Si-H units are possible in plasma-deposited a-Si:H. However, crystalline $\langle 111\rangle$ Si reconstructs to give parallel first-neighbor dangling bonds and sublayers of odd-membered rings.[35] If a-Si bears any resemblance to this, post-hydrogenated a-Si may contain more *cis* Si-H configurations.

III. DOPANT STATES

A. Calculations

Four different situations are used to model possible dopant-hydrogen interactions: the hydrogenated vacancy, the two layer models, and also a network

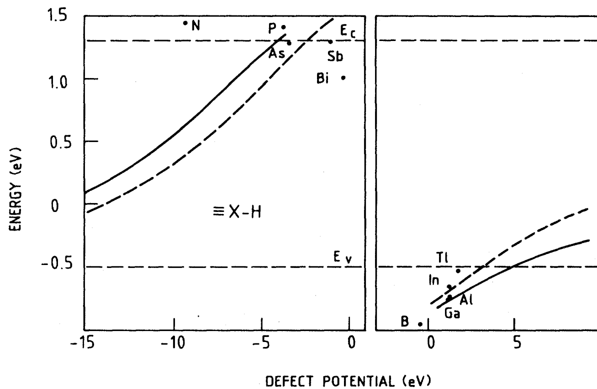

FIG. 6. Impurity levels of hydrogenated dopant sites modeled by the hydrogenated vacancy. The solid line is the impurity characteristic of dopants of the same radius as Si. The dashed line is that of unhydrogenated dopant sites for reference (also in Figs. 7—9). Energies are given with respect to the band edges of c-Si; those of a-Si:H lie at −0.5 and 1.3 eV.

which is randomly hydrogenated away from the dopant site. The dopant levels of isolated $\equiv X$—H units are most easily modeled using the HV, as in Fig. 6. The silicon adjacent to the dopant is converted into the hydrogenated vacancy (Fig. 1) giving a paired defect, similar to those discussed earlier.[1,36] Its symmetry is lowered from T_d to C_{3v}. Its a_1 levels are derived from the HV A_1 state, the dopant's s and axial p states. These levels are related to the parent A_1 level but can be strongly modified. The e levels of the pair defect correspond to the π orbitals normal to the X—H axis. They are related to the parent T_2 levels and are also modified as the HV has no π interaction, unlike in the true paired-defect case.[36] The donor levels have a_1 symmetry and the acceptor levels have e symmetry. They are both slightly shallower than those of the unhydrogenated site. The effects of variations in the dopant size can be described by changing the off-diagonal elements

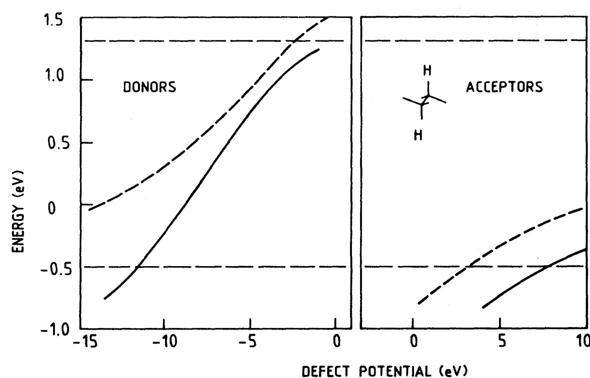

FIG. 7. Impurity levels of hexagonal SiH.

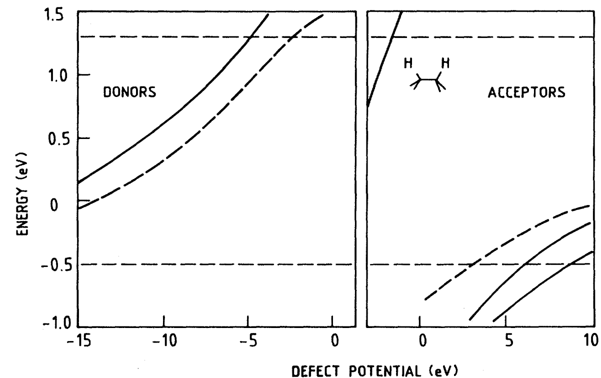

FIG. 8. Impurity levels of orthorhombic SiH.

of the defect matrix and assuming a inverse square of the bond-length scaling.[1] The size effect is marginally larger for $\equiv X$—H sites because one of the four bonds is X—H which has proportionately larger length changes. As in I, smaller dopants are found to give shallower levels. Thus isolated $\equiv X$—H units behave similarly to their parent units with four bonded Si atoms, and if anything, are better dopants.

The dopant levels of adjacent $\equiv X$—H and $\equiv$Si—H units can be studied using the two SiH lattices. Each Si site in hexagonal (D_{3d}) SiH has C_{3v} point-group symmetry and the defect levels belong to the a_1 and e representations. Figure 7(a) shows the a_1 donor level to be deeper than that of the unhydrogenated site. The acceptors are e-like and much shallower than for the unhydrogenated site. The a_1 (p_z) acceptor level lies much deeper in the valence band and is always occupied.

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The dopant spectra for the orthorhombic SiH lattice are shown in Fig. 8. The site symmetry is C_{1h}. The A'' or π states have odd parity leaving the s, axial p, and the remaining π-like p states with A' symmetry. The acceptor levels in Fig. 8(b) are simpler, the highest is the A'' π state which is still shallower than for an unhydrogenated site. The donor levels are unusual. Two A' levels are found, with the p-like curve lying below the s-like curve. Thus deep donors in this configuration occupy p states. Both curves lie above that for donors at unhydrogenated sites, so this unusual effect is unlikely to be observed experimentally.

We also investigated the effect of hydrogenating

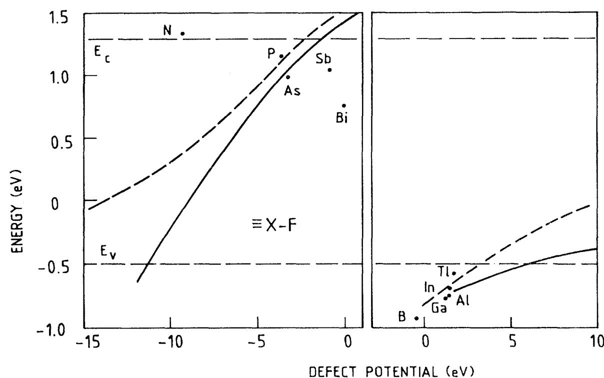

FIG. 9. Impurity levels of the fluorinated vacancy.

the network while leaving the dopant site itself bonded to four silicons. The dopant site retains its T_d symmetry, at least locally. Hydrogenation was effected by breaking Si—Si bonds randomly and tying off with two hydrogens which are forbidden to interact with each other. The defect levels and local DOS were calculated using the recursion method. As expected, the valence band retreats, even in the local DOS at a $Si(Si_4)$ site. The donor levels are little changed. The acceptor levels are found to fall in energy at a similar rate to the retreat of the valence-band edge. Thus hydrogenation does not leave acceptor levels of unhydrogenated sites high and dry, above the retreating valence band.

Finally, the impurity levels of the fluorinated vacancy are shown in Fig. 9. The fluorinated vacancy is formed in an analogous fashion to the HV, as described in the Appendix. It is a simple method to find the impurity levels of single $\equiv X$—F units. The donor levels are seen to be nearly 0.1 eV deeper than for the basic $\langle 4 \rangle$ site, but acceptors are slightly shallower. The Si—F bond is both polar and strongly covalent. The deepening of the donor levels can be understood by considering paired defects. Smaller, more strongly bonded spectators were found to give shallower levels. Highly electronegative spectators were found to deepen donor levels because they increased an effective defect potential. The two effects oppose each other for a fluorinated vacancy, and clearly the electronegativity effect is the larger. The F p-orbital energy was fitted to photoemission data on a-Si:F (Ref. 37) because of its important effect on these donor levels.

B. Discussion

The energies of dopant levels depend on both the symmetry and type of local bonding. The symmetry of a $\equiv X$—H site is reduced to C_{3v} or lower, which splits the degeneracy of p states and allows coupling between the s and axial p orbitals. Our results emphasize that the splitting of p levels is much more important than the coupling. In most cases donors move slightly but retain their s character. The highest acceptors are generally π-like with the axial p level lying much deeper in the band. Although crystallographically $\equiv X$—H sites have reduced symmetry, chemically they are still tetravalent. Replacing Si with H is a moderate chemical perturbation, but the only major effect is to lower the energy of states involving the axial p orbital which then is not important for impurity states near the gap.

In specific configurations, our results for the HV show the isolated $\equiv X$—H site to be an excellent dopant. Also, the depth of dopant levels for sites with four Si neighbors change little with progressive hydrogenation of the network. In general, the more marked changes occur when a $\equiv X$—H unit is adjacent to a $\equiv$Si—H unit, as this lowers the site symmetry further. The acceptor levels appear to remain shallow, dropping as quickly as the valence edge, but donor levels can be deeper.

Our results indicate $\equiv X$—F donor units to be slightly deeper. We also find the conduction edge to rise with fluorination, unlike in the case of hydrogenation where it merely changes character. Thus we find fluorination to have a slightly detrimental effect on n-type doping. Experimentally, a-Si:(F,H) has a higher ultimate n-type conductivity than a-Si:H (Ref. 12), which we suggest must be due to a steeper conduction-band tail rather than improved donor activity.

IV. METASTABILITIES

A variety of metastable phenomena occur in a-Si:H—photoinduced reductions in the dark and photoconductivity (the Staebler-Wronski effect),[14] a photoinduced change in the long-term dark ESR signal,[15] and a reversible field-induced change in apparent doping efficiency.[16] The Staebler-Wronski effect is now generally believed to be a bulk effect and may be related to changes in the density of deep gap states.[21] Hydrogen is known to be mobile in a-Si:H and can passivate dangling bonds after deposition.[38] The metastabilities could be related to the breakage of remaining weak Si—Si bonds and their subsequent passivation. It is also possible that hydrogen migration might convert shallow dopant states to deeper states, but our calculations tend to rule out this type of mechanism. We find that changing the neighbor atoms rarely move impurity energies by 0.5 eV. Such movements require coordination changes.

Hydrogen diffusion and variable compensation have been suggested as possible sources of field-induced doping[21] but we show that neither can ex-

TABLE I. Interactions for Si—H and Si—F bonds in eV [Si orbitals first in $V(sp)$ etc.].

	$E(s)$	$E(p)$	$E(p^*)$	$V(ss)$	$V(sp)$	$V(ps)$	$V(pp\sigma)$	$V(pp\pi)$	$V(pp^*\sigma)$
H	−3.38		6.7	−3.52		3.22			2.46
F		−9.0			−5.75		5.75	1.5	

plain its magnitude. Electric fields appear able to produce a differential shallow dopant concentration over a factor of 10 larger than the steady-state value. Doping efficiencies in a-Si:H are now believed to be of order 1% or less.[39] The results here and in paper I show that dopants at ⟨4⟩ sites give essentially shallow levels and, except for B, give no gap states at undistorted ⟨3⟩ sites. In particular, ⟨4⟩ sites cannot possess two types of states, one which is electronically active but rare and another more common state which only becomes activated by high electric fields.

Our results suggest that coordination changes of the dopants are required to explain the size of the field-induced doping effect, and the most natural explanation involves Street's theory of Fermi-level controlled doping efficiency.[39] Street proposes that dopant coordinations change in response to the position of ϵ_F, such that while charged ⟨4⟩ dopant sites are allowed, neutral ⟨4⟩ dopant sites are not, as the latter break the 8-N coordination rule. Attempts to occupy the dopant level and give a neutral site are countered with bond breakage, producing ⟨3⟩ alloying sites and Si dangling bonds. The attraction of this mechanism is that it involves a large fraction of dopant atoms and explains the size of the field-induced doping effect without requiring a huge reservoir of "passive" ⟨4⟩ sites. This mechanism implies that the effect may not be totally reversible as bond reformation may be more difficult due to the overconstrained nature of the network for Si.[11]

V. CONCLUSIONS

The electronic structure of many Si-H, Si-F, dopant-H, and dopant-F configurations have been calculated. Generally, monohydrogenated ⟨4⟩ dopant sites have been found to be as shallow as those sites with four Si neighbors. Monofluorination of a substitutional donor site slightly deepens its level. Summarizing papers I and II, we have found no monohydrogen or dopant configurations which give additional deep states near the gap center. It is pointed out that hydrogenation erodes the upper valence band by a maximum of about 0.7 eV (equal to the $pp\pi$ interaction) if only Si—H units are present.

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APPENDIX A: TIGHT-BINDING INTERACTIONS

This Appendix describes the parametrization of the Si-H and Si-F interactions. Restricting the interactions to only first neighbors removes the need for further assumptions of the bond-length dependence of second-neighbor interactions when used in amorphous systems. First neighbor parametrizations are inherently more easily transferable.

The Si-H parameters are found by fitting the energies of the SiH_4 molecule using sp^3s^* orbitals on Si and sp^* orbitals on H. SiH_4 has T_d symmetry and σ and σ^* A_1 and T_2 states. The mean energies of the A_1 and T_2 states are inconsistent with the s-p splitting used in Si. Pandey[40] allows the possibility of a $V(\mathrm{H}s,\mathrm{H}s)$ interaction to lower T_2 energies. We adopt the alternative philosophy and suggest that the antibonding T_{2u} state is repelled downwards by the excited Hp^* orbital. The parameters are simplified by allowing Hp^* to interact only with Sip orbitals. As in bulk Si, we take the Sis^* orbital to interact only with unexcited p orbitals, of which H has none. The A_1 energies are used to set $E(\mathrm{H}s)$ and $V(ss)$. The T_{2g} state sets $V(sp)$ and then $V(sp^*)$ is used to reproduce the T_{2u} level.

We suggest that the electronic structure of monovalent H is often better represented by including the p^* or $2p$ level than by using higher-order H-H interactions. Nearest-neighbor parametrizations generally portray the bands of homopolar semiconductors reasonably accurately.[41] Higher interactions depend not only on atomic separations but also on orthogonality to any intervening atoms, as is readily seen in the chemical pseudopotential formulation.[42] Thus, additional calculations or assumptions are needed to use higher-order interactions in the presence of angular distortions in a-Si. This applies equally to the H-H interactions in a-Si:H. We suggest that direct interactions should only be included between hydrogens without a common bonded Si,

such as across the hydrogenated vacancy or an internal surface. In contrast, including the H $2p$ orbital gives correct electronic energies in a number of Si-H systems. It also reproduces the polarized charge density of its covalent bonds.[43] Our parametrization only specifies the σ symmetry of the excited orbital, it is identified as $2p$ from these bonding arguments.

The Si-F parameters are adapted from the Si-O interactions in SiO_2 (Ref. 44) by scaling them as the inverse square of the bond length. The energy of the Fp orbital is set at -9 eV. This places the F$p\pi$ orbitals of a-Si:F about 9 eV below the valence maximum as observed in photoemission.[37] Atomic radii are tabulated in paper I and the interactions are collected in Table I.

APPENDIX B: HYDROGENATED VACANCY

Equivalent A_1 (s) and T_2 (p) orbitals are found for the hydrogenated vacancy by taking linear combinations of the s (and p^*) orbitals on each hydrogen i:

$$|A_1\rangle = 0.5(|1\rangle + |2\rangle + |3\rangle + |4\rangle) ,$$

$$|T_2,x\rangle = 0.5(|1\rangle + |2\rangle - |3\rangle - |4\rangle) .$$

We then define equivalent interactions:

$$E'(A_1) = E(H,s), \quad E'(T_2) = E(H,s) ,$$

$$V'(s,A_1) = 0.5V(ss) ,$$

$$V'(p,A_1) = 0.5V(ps) ,$$

$$V'(p,A_1) = 0.866V(ss) ,$$

$$V'(p,T_2\sigma) = 0.866V(ps) ,$$

$$V'(p,T_2\pi) = 0 .$$

The fluorinated vacancy can be handled in a similar fashion after simplification. Fluorine is monovalent in a-Si, forming a single σ bond with its one singly occupied p orbital. The four orbitals at the vacancy site can only be replaced by four fluorine-related orbitals. Thus the $p\sigma$ orbital of each F is retained and the less important $p\pi$ and s orbitals are dropped. The equivalent $|A_1\rangle$ and $|T_2\rangle$ orbitals can be formed by taking linear combinations, such as for the HV.

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*Present address: Central Electricity Research Laboratory, Leatherhead, Surrey KT22 7SE, United Kingdom.

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