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Doping mechanism in *a*-Si:H

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A bonding mechanism is developed to account for the unique features of substitutional doping of hydrogenated amorphous silicon (*a*-Si:H) by trivalent elements. Following Street we argue that doping is produced by dopant—valence-alternation pairs (DVAP's) consisting of an ionized substitutional dopant and an oppositely charged Si dangling bond. We argue that DVAP's are stabler than simple substitutional sites because of their diamagnetism, having no unpaired bonding or antibonding electrons. DVAP's are an excited configuration of the electrically inactive ground state of the dopant in the random network, the threefold-coordinated site, which obeys the $8-N$ rule and we note that dopants are accommodated substitutionally in crystalline Si because both the DVAP and the threefold site are topologically forbidden. We also show that the DVAP has a negative U, accounting naturally for the saturation of doping efficiency and the strong increase in dangling-bond density found experimentally. We relate the diamagnetism of DVAP's to the general defect bonding in amorphous semiconductors of groups IV—VI. Modulation doping using superlattices is noted to produce doped *a*-Si with lower defect density.

I. INTRODUCTION

If crystalline (*c*-) Si is doped with, for instance, phosphorus, each P atom is constrained to be tetrahedrally coordinated and substitutional, so its fifth electron is unbound and produces doping. Amorphous semiconductors are not so constrained, so each atom generally satisfies its normal valence requirement locally by obeying the $8-N$ (octet) rule[1] relating coordinations N_c to the element's valence number, N, viz., $N_c=8-N$ for $N\geq 4$ and $N_c=N$ for $N<4$; thus P is expected to be threefold coordinated whatever its environment, and doping should not occur. Consequently, the substitutional doping of hydrogenated amorphous silicon[2] (*a*-Si:H) by P, B, etc., was somewhat surprising and clearly our understanding of bonding in covalent networks is incomplete.

A theory must account for distinct features of doping in *a*-Si:H.

(i) Substitutional sites, P_4 for phosphorus, coexist with electrically inactive threefold P_3 sites so the doping efficiency is less than unity.[2]

(ii) E_F cannot be moved into extended states at high doping levels, so doping saturates and degenerate conduction is not found.

(iii) A residual dangling-bond density remains, and increases dramatically in doped samples.[3,4] These dangling bonds cannot be removed simply by improving the deposition technique but appear to be intrinsic to the doping mechanism of *a*-Si:H. Interestingly, their density depends on the position of E_F rather than the overall doping level because it decreases again for compensated doping.[3]

(iv) Doping predominantly generates paired spins; no electron spin resonance (ESR) associated with dopants has been found,[5] and the ESR usually associated with carriers in tail states remains quite small in darkness,[3] unlike that of free carriers in *c*-Si or even microcrystalline Si.[6]

(v) Doping has been observed in *a*-Si containing little or no hydrogen,[7] so while hydrogen has an important beneficial effect in reducing the density of gap states associated with Si dangling bonds, it is unlikely to be central to the doping mechanism itself, or the breaking of the $8-N$ rule.

In this paper we show how the ionized dopant mechanism of Street[8] accounts for these features. We then rationalize the breaking of the $8-N$ rule and further show that the mechanism is consistent with a general scheme of defect bonding which is valid for amorphous semiconductors of group-IV to -VI elements.

II. VALENCE ALTERNATION THEORY OF DOPING FOR *a*-Si:H

At the neutral substitutional site P_4^0, four of the five P electrons are in bonds while the fifth electron is unpaired and lies in a shallow donor level in *c*-Si (Fig. 1). Street[8] suggested that the unusual features of doping in *a*-Si:H could be explained if the donors were always ionized as P_4^+ so that E_F lay below the donor level. He further proposed that the released electron entered a dangling bond, giving Si_3^-.[8] Consequently, as E_F never enters the donor levels, this automatically prevents degenerate conduction, and as the dangling-bond density must equal the number of substitutional donors this also accounts for the rapid increase in their density, so satisfying points (ii)—(iv).

The differences in the doping mechanism in *c*-Si and *a*-Si:H result from the different effects of topological constraints on the three dopant configurations (Fig. 2). P_3^0 is the most stable configuration of P in an unconstrained network. It is now clear that the P_4^+-Si_3^- pair is the next most stable configuration in a network and that P_4^0 has a still higher energy. The P_4^+-Si_3^- pair will be called a dopant—valence-alternation pair (DVAP) because it is formed from the ground state by valence alternation:[5,9,10]

$$P_3^0+Si_4^0\rightleftharpoons P_4^+ + Si_3^- \ . \qquad (1)$$

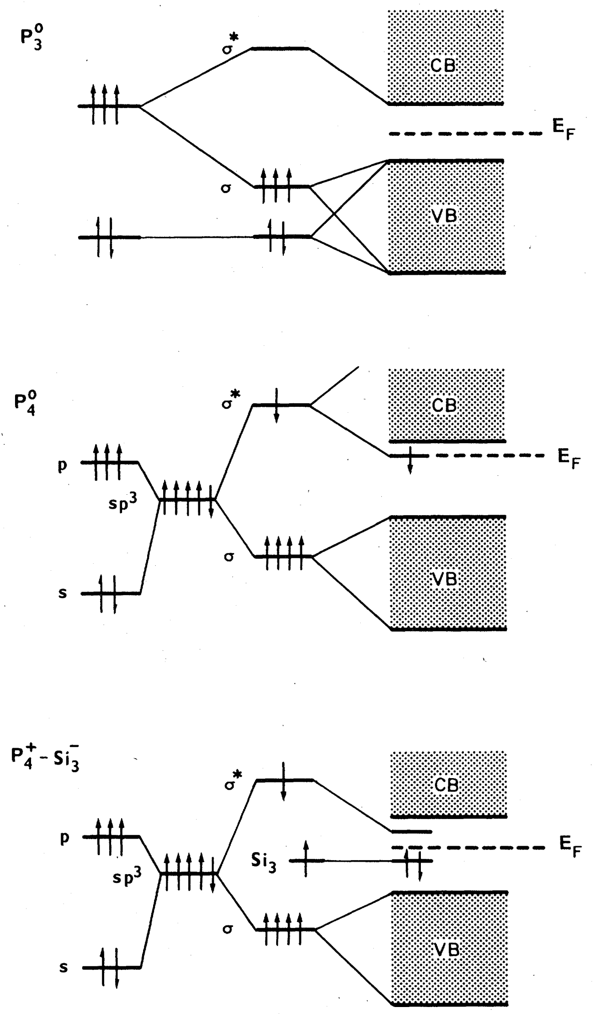

FIG. 1. Electronic configurations of P_3^0, P_4^0, and P_4^+-Si_3^-. VB and CB denote valence and conduction bands, respectively.

Thus doping of a-Si:H is due to an excited configuration of P_3^0. It is clear from Fig. 2 that both P_3^0 and the DVAP are topologically forbidden in c-Si, so P is forced to enter as P_4^0. Hence the differences between doped a-Si:H and c-Si arise because dopants can adopt lower-energy configurations in random networks than are possible in crystals.

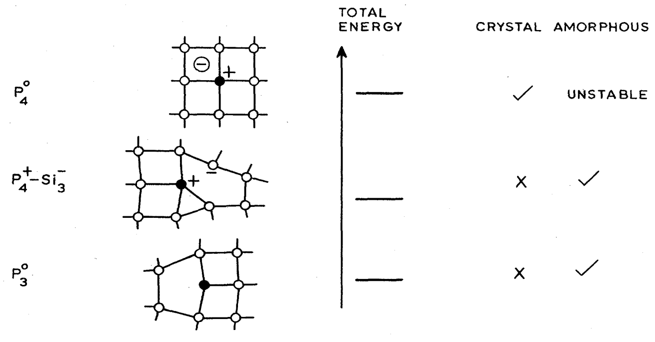

FIG. 2. Configurations, total energy, and stability in c-Si and a-Si:H of P_3^0, P_4^+-Si_3^-, and P_4^0 sites.

The DVAP has been shown[9] to possess a negative effective correlation energy (U), as do the valence-alternation pairs (VAP's) in chalcogenide glasses.[10] U is negative because the generalized defect reaction,

$$2D^0 \rightarrow D^+ + D^- \tag{2}$$

or

$$2Si_3^0 + P_3^0 \rightarrow P_4^+ + Si_3^- + Si_4^0 , \tag{3}$$

is exothermic. This is because Si_3^+ overcoordinates with P_3^0 in doped a-Si:H while it cannot with Si_4^0 in undoped material. Thus $U > 0$ in intrinsic a-Si:H but $U < 0$ for DVAP's in doped a-Si:H. The P_4 levels lie just below E_c (Fig. 1) and the Si_3 levels around midgap.[9] The requirement that P_4^0 does not form is equivalent to E_F always lying below the P_4 levels which in turn is equivalent to the familiar pinning of E_F between the D^+ (P_4) and D^- (Si_3) states of the negative-U centers—i.e., the negative U is a general description of the saturation of doping efficiency of a-Si:H at high doping levels. Note, however, that the valence alternation occurs only during deposition in a-Si:H rather than at all times as in chalcogenides.

The efficiency, η, of the DVAP doping mechanism is found by applying the law of mass action and charge neutrality[8] to equilibrium (1):

$$[P_4^+] = [Si_3^-] = n , \tag{4}$$

$$K_1 = \frac{[P_4][Si_3]}{[P_3^0]} = \frac{n^2}{N-n} , \tag{5}$$

so

$$\eta = n/N \simeq KN^{-1/2} \tag{6}$$

if $n \ll N$. In contrast, if doping is due to P_4^0 centers in equilibrium with P_3^0 sites, the equilibrium constant would be

$$K' = \frac{[P_4^0]}{[P_3^0]} \tag{7}$$

giving

$$\eta = K' . \tag{8}$$

Thus a pair-doping process gives an efficiency declining with the doping level, while a single-site process leads to a constant doping efficiency. Early experimental estimates of η assumed that the density of gap states was independent of doping level and equated n to the integrated density of states between the position of E_F in undoped and doped samples.[2] As we now realize that gap states have a variable density, η has been estimated by assuming equality (4) and measuring the total density of dangling bonds by ESR and light-induced ESR.[3,8] This verified the $N^{-1/2}$ dependence of η.

A finite density of DVAP's will be present at elevated temperatures, and we expect some density to be quenched into a-Si:H during deposition, in a similar manner than VAP's are believed to be quenched into chalcogenide glasses in cooling through the glass transition temperature.[10] The DVAP creation energy can be estimated from K_1 in these circumstances:[11]

$$K_1 = \exp(-E/kT_d) \ . \tag{9}$$

Taking the fictive temperature to be the deposition temperature, for example $T_d = 250\,^\circ\mathrm{C}$, we estimate $E = 0.8$ eV for Si:P using the concentration dependence of η quoted by Street.[8]

The success of the DVAP model is its consistent interpretation of a wide body of data. It explains the changeover from doping to alloying behavior in a-Si$_{1-x}$P$_x$:H for increasing x without additional assumptions. It accounts naturally for the strong increase in Si dangling-bond density seen by ESR and light-induced ESR.[3] Dangling bonds are the dominant recombination and trapping center and their increased density causes a dramatic reduction in the efficiency of the 1.4-eV luminescence[3] and the minority carrier lifetime[12–14] with doping level, according to a $N^{1/2}$ law.[15] The increased density is also seen optically[16] and by deep-level transient spectroscopy (DLTS).[17]

Alternative models of doping[18–20] do not account for the presence of dangling bonds. For instance, the absence of degenerate conduction could be attributed to the dopant levels lying quite deep in the gap of *a*-Si:H, thereby preventing E_F approaching the band edges.[18] Similarly, the stability of $\mathrm{P_4}^0$ and $\mathrm{B_4}^0$ sites and the breaking of the $8-N$ rule could be attributed to the stabilizing effect of finite bandwidths,[19] but neither suggestion provides a complete theory. Finally, electrical activity has been attributed to gap states of $\mathrm{P_3}$ and $\mathrm{B_3}$ sites.[20] However, $\mathrm{P_3}^0$ and $\mathrm{B_3}^0$ sites are not expected to give gap states for their stable bond angles; the nonbonding state of $\mathrm{P_3}^0$ is *s*-like and lies deep in the valence band (Fig. 1) (Ref. 21) while the nonbonding state of planar $\mathrm{B_3}^0$ is *p*-like and lies just above the conduction-band edge. Also ESR signals from dopants have yet to be observed but would be expected from ionized dopants in this model.

Further evidence on the DVAP mechanism is provided by the behavior of compensated samples. Boron doping creates positively charged dangling bonds:

$$\mathrm{B_3}^0 + \mathrm{Si_4}^0 \rightleftharpoons \mathrm{B_4}^- + \mathrm{Si_3}^+ \ , \tag{10}$$

but dangling bonds need not be created for fully compensated doping:

$$\mathrm{P_3}^0 + \mathrm{B_3}^0 \rightleftharpoons \mathrm{P_4}^+ + \mathrm{B_4}^- \ . \tag{11}$$

The equilibrium constant for this reaction is

$$K_3 = \frac{[\mathrm{P_4}^+][\mathrm{B_4}^-]}{[\mathrm{P_3}^0][\mathrm{B_3}^0]} \ . \tag{12}$$

A constant K_2 similar to K_1 can also be defined for the boron reaction (10). The density of dangling bonds and η now depends on K_1, K_2, and K_3. If $K_3 > K_1 + K_2$, low dangling-bond concentrations will be present in compensated samples, in accord with luminescence and ESR data.[3,4]

Modulation doping of an *a*-Si:H,N superlattice[22] might produce direct evidence for the DVAP mechanism. In crystalline superlattices, layers of doped wide-gap semiconductor will dope intrinsic narrow-gap layers by charge spillover. In an *a*-Si:H superlattice, defects are created in the doped layers according to the DVAP model. Superlattices offer the opportunity of doping with less degradation by defects, as conduction occurs in the intrinsic layers. A reduction in defect absorption has been observed, but so far only in samples with a strange doping process.[23]

Hydrogenation was crucial for the first observations of doping in *a*-Si, due to its passivating effect on gap states. A further, direct role of H in the doping mechanism could be proposed, to reduce the average coordination and network strain, thereby permitting a minority of dopants to increase their coordination at substitutional sites. However, recently, almost hydrogen-free *a*-Si has been doped,[7] so we maintain that H itself does not allow the $8-N$ rule to be broken. NMR data[24] suggest H clustering around $\mathrm{P_4}$ sites. The DVAP model includes this effect by allowing K_1 to differ for $\equiv$P— and $\equiv$P—H sites, and similarly for any B,H clustering.[25]

A defect mechanism is probably also involved in the interstitial doping[26] of *a*-Si:H. Li always ionizes, so no equilibrium is involved:

$$\mathrm{Li} + \mathrm{Si_4}^0 \rightarrow \mathrm{Li}^+ + \mathrm{Si_3}^- \ .$$

The doping efficiency is now unity but the presence of $\mathrm{Si_3}^-$ still prevents E_F entering extended states.

The DVAP model successfully accounts for most features of the gap-state spectrum of *a*-Si:H.[9] The $\mathrm{P_4}$ and $\mathrm{B_4}$ states are taken to be energetically quite close to their respective band edges and the $\mathrm{Si_3}$ levels placed at midgap as seen experimentally.[4,14,17,27–29] It was necessary to distinguish between deep and shallow gap states.[9] Deep states were defined as those whose energy depended on coordination and included those due to dopants and $\mathrm{Si_3}$ sites. These states could have positive or negative U. Shallow states, like the tail states, depend little on coordination and always have $U > 0$, as seen experimentally.[29]

The DVAP model does not, however, account for the extra deep states found around by luminescence[3] and DLTS (Ref. 30) in compensated samples around $E_v + 0.5$ eV. These could be dopant complexes, but likely configurations have been calculated to yield no gap states,[18] or intrinsic spinless defects such as those discussed by Adler.[5]

III. DOPANT AND DEFECT BONDING IN AMORPHOUS SEMICONDUCTORS

The novel doping mechanism of *a*-Si:H and defects of amorphous semiconductors can now be rationalized in a single framework by concentrating on the wave-function character of their gap states. We recall that the basis of the $8-N$ rule is that bonding energy is maximized by occupying only states of bonding (σ) character while keeping empty those of antibonding (σ^*) character. Sites generally also possess nonbonding states which do not change energy during bonding and so their occupation does not affect the total bonding energy. Maximizing coordination then gives the $8-N$ rule. The different coordinations of defects produces a strong, short-ranged perturbation which introduces states deep in the gap and their very localized wave functions concentrate their contributions to the total energy onto the defect site itself. Thus defects tend to obey an "occupation principle" to minimize their energy: "stable configurations have maximum coordination so that any deep gap states of bonding character are full, any of antibonding character are empty while nonbonding states can have any occupation." We see that deep states are usually diamagnetic and unpaired electrons are only permitted in nonbonding states, i.e., dangling bonds or lone pairs. Thus *networks are predominantly diamagnetic* as proposed by Anderson,[31] with paramagnetic states appearing only in unusual circumstances such as by excitation or sometimes intrinsically[32] to relieve strain as in *a*-Si:H. The principle can also be expressed as a "modified $8-N$ rule" where N is now the actual number of electrons at the site.

Considering defects in chalcogens, for example, Se, $\mathrm{Se_1}^-$ possesses a full nonbonding (π) gap state. D^+ must be $\mathrm{Se_3}^+$ rather than $\mathrm{Se_1}^+$ to maximize coordination and so possesses an empty σ^* gap state. Adding electrons to $\mathrm{Se_3}^+$ would cause occupation of the σ^* state. Instead the bond breaks, giving $\mathrm{Se_1}^0$, converting the σ^* state to π which is allowed to be partially occupied. Thus the principle requires D^0 to be $\mathrm{Se_1}^0$ rather than $\mathrm{Se_3}^0$ as found by ESR (Ref. 33) and total-energy calculations.[34] Similarly for pnictides, $\mathrm{P_4}^+$ has an empty σ^* state, $\mathrm{P_2}^-$ a full π state, while D^0 is $\mathrm{P_2}^0$ rather than $\mathrm{P_4}^0$ as the partially occupied state is now π-like. In *a*-Si:H the dangling bonds are nonbonding and so can have any occupation.

The origin of the stability of DVAP's such as $\mathrm{P_4}^+$-$\mathrm{Si_3}^-$ compared to neutral substitutional sites $\mathrm{P_4}^0$ is now much clearer. $\mathrm{P_4}^0$ sites involve the partial occupancy of σ^*-like states, while in DVAP's these are empty. The only occupied states are σ and nonbonding states. The stability of DVAP's can also be attributed to the conservation of bonds in valence alternation, Eq. (1). The DVAP is likely to be more stable because it involves the replacement of one σ and one σ^* electron at $\mathrm{P_4}^0$ by two nonbonding electrons at $\mathrm{Si_3}^-$, recalling that σ^* states are more repulsive than σ states are attractive. Similarly for boron, $\mathrm{B_3}^0$ has a partially occupied σ-like state while the $\mathrm{B_4}^-$-$\mathrm{Si_3}^+$ DVAP has full σ states and an empty nonbonding state. Thus bonding at defects and impurities in amorphous semiconductors of groups IV, V, and VI are for the first time expressed in a single conceptual framework.

IV. CONCLUSIONS

We showed that the doping species of phosphorus in *a*-Si:H is the charged pair $\mathrm{P_4}^+$-$\mathrm{Si_3}^-$ rather than the simple substitutional site $\mathrm{P_4}^0$, because the pair has a lower energy in an unconstrained network. A crystal is constrained by periodicity so only $\mathrm{P_4}^0$ is possible. The charged pair is a valence alternation pair which has a negative U. Thus we find $U<0$ for dopants but $U>0$ for undoped *a*-Si:H. We accounted for the breaking of the $8-N$ rule and showed that the bonding at defects and impurities can be described within a single conceptual framework, which applies equally to chalcogenides and Si, to negative- and positive-U systems.

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