Normal Structural Bonding and Defects in Covalent Amorphous Solids*

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Although the 8-N rule of covalent bonding is generally obeyed in amorphous semiconductors, well-defined defect centers exist and these control the electronic properties of the solids. The defects have two distinct reasons for their presence—they can arise from either strains upon material preparation or thermodynamic considerations. The strain-related defects characterize those amorphous solids in which the average coordination number is larger than approximately 2.4; their concentration is ordinarily very sensitive to the preparation techniques. In contrast, thermodynamically induced defects arise because of their low creation energy, and a minimum concentration characterizes any given material. These ideas have led to a resolution of several major puzzles with regard to the electronic properties of the two major classes of amorphous semiconductors—chalcogenide glasses and amorphous silicon-based alloys. Pure amorphous silicon is overconstrained and has large defect densities, but these can be reduced by many orders of magnitude if the material is alloyed with monovalent atoms such as hydrogen or fluorine. On the other hand, amorphous As_2Se_3 always contains a high defect density, for thermodynamic reasons. In addition to the concentration of defects present in a given material, its electronic properties depend critically also on the *nature* of these defects. In particular, the sign of the effective correlation energy of the defect with the lowest creation energy is of the utmost importance.

Introduction

The electronic structure of amorphous solids represents an important example of an area in which the conventional approach of solid-state physics fails, and a chemical viewpoint is essential from the very beginning. Because the usual elegant techniques involving use of group theory, Brillouin zones, k-space, and Bloch states cannot be applied to any system which lacks long-

range order, it has been said that a solid-state physicist without periodicity is like a psychiatrist without a couch. Fortunately, a solid-state chemist without periodicity is more like a fish without a bicycle.

In principle, a proper analysis of the problem of either a crystalline or an amorphous solid should begin in the same way as that of a molecule, with a solution of the many-body Hamiltonian of the system. This Hamiltonian is simple to write down, consisting of the kinetic energies of all of the outer electrons and all of the ion cores and the sum of all the electrostatic attractions and repulsions. It is significant that the many-body Hamiltonian cannot distin-

guish between the crystalline and amorphous phases of a solid of the same composition, just as it cannot distinguish between structural isomers in a chemical problem. Our computational abilities at present are enormously short of being able to solve for the lowest-energy states of any complex Hamiltonian, so an empirical approach is always used. A major simplification is the *adiabatic approximation*, a first-order expansion in the small parameter $(m/M)^{1/4}$, where m is the electronic mass and M is an average ion-core mass, typically a factor of 10^5 larger. This approximation effectively separates the problem into three subproblems: (1) *structure*, i.e., finding the equilibrium positions of the ion cores; (2) *phonons*, i.e., finding the normal modes of oscillations of the ion cores about their equilibrium positions; and (3) *electronic structure*, i.e., evaluating the states available to the electrons, under the assumption that the ion cores are in their equilibrium positions. The structure is always determined empirically, via the results of diffraction studies. These results are then the starting point for an analysis of the other two problems. Calculation of the electronic structure is also too difficult to handle without a major simplification, in this case the *one-electron approximation*, in which it is assumed that each electron moves in the average field of all of the others. The adiabatic approximation neglects interactions between electrons and phonons; these can be explicitly reintroduced at a later point in the analysis. The one-electron approximation neglects the possibility that electrons can correlate their motion in order to minimize their electrostatic repulsion; the effects of these *electronic correlations* can also be analyzed at a later point. The latter approximation enables us to introduce the density of states $g(E)$, which is the number of one-electron states per unit volume per unit energy available to electrons moving through the solid. If we further assume that, due to screening

effects, the electrons interact with each other on the average only weakly, then $g(E)$ taken together with the Fermi–Dirac distribution function,

$$f(E) = \{\exp[(E - \epsilon_F)/kT] + 1\}^{-1}, \quad (1)$$

where ϵ_F is the Fermi energy, yield the electrical and optical properties of the material in a straightforward manner.

In amorphous materials, the absence of long-range periodicity makes it more difficult to determine the overall structure, but the results of diffraction and other experiments, such as infrared, Raman, and EXAFS (extended X-ray absorption fine structure), taken together with a knowledge of the chemistry of the constituent elements usually lead to reliable conclusions. On the other hand, the effects of disorder on the *nature* of the electronic states often requires a more sophisticated analysis in order to interpret the electrical transport properties of amorphous solids. In this paper, I briefly discuss the structure of amorphous solids, paying attention to both the normal structural bonding which reflects the underlying chemistry, and the variations from this bonding which can have either a thermodynamic or a mechanical origin. The modifications of conventional solid-state theory necessary to understand the electronic behavior are then discussed in detail.

Structure of Amorphous Solids

Empirical studies show that although amorphous solids do not exhibit any long-range order, there is a great deal of *short-range order*. A typical result is shown in Fig. 1, which represents the electron-diffraction results of Moss and Graczyk (*1*) comparing amorphous and crystallized silicon films. The similarities between the first peaks of the two structures show that the average coordination number is close to 4 in both, and the average bond lengths are also
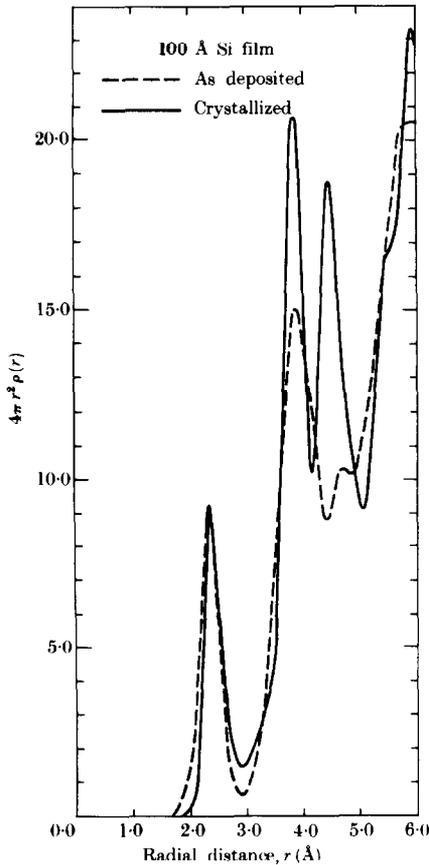
FIG. 1. Radial distribution function of an evaporated amorphous-silicon film 100 Å thick compared with that of crystallized silicon. (From Moss and Graczyk, Ref. (*1*)).

the same, 2.35 Å. But, in addition, there is a great similarity between the second peaks in the two films, reflecting a constraint on the bond angles. The average number of second neighbors remains approximately 12 in the amorphous film, but some disorder broadening of the second peak relative to that in the crystal indicates a spread in bond angles of about ±10°. In contrast, there is little or no evidence for the third or any higher peaks in the amorphous film, suggesting a great deal of dihedral-angle and longer-range disorder.

In general, amorphous solids possess the same nearest-neighbor configuration as that of the corresponding crystal, since this reflects the same strong chemical forces operating in both types of solid. In primarily covalent amorphous materials, there are also great similarities in the second-neighbor configuration, again reflecting the chemistry of covalent bonding, viz., fixed bond angles. In some amorphous solids, e.g., Se (*2*), there is evidence for *intermediate-range order*, suggesting constraints on dihedral angles and even beyond.

Much of the structural results can be understood in terms of simple chemistry, taken together with the constraints of network topology. Ionic solids maximize their cohesive energy by optimizing their Madelung potential, the electrostatic attraction between the array of charged ions (treated as point charges). Thus the optimal structure is a central cation surrounded by as many anions as is consistent with the composition and the geometric constraints relating to prevention of significant overlap of the electronic charge on different anions. If the anions are not much larger than the cations, then 8 is the optimal coordination of a simple AB ionic solid, but this number drops to 6 and ultimately to 4 as the ratio of anion to cation size increases. If Z is the average coordination number in the solid, the sharp variations in energy with bond lengths (evident from the large observed bond-stretching vibrational frequencies) leads to $Z/2$ constraints per atom (since each bond involves two atoms). Ionic bonds generally do not require a fixed band angle, so that the fact that every atom has three degrees of freedom suggests that the number of constraints is less than the number of degrees of freedom, provided that

$$Z \leq 6. \qquad (2)$$

We thus can conclude that amorphous networks are difficult to attain for solids that crystallize in the CsCl structure ($Z = 8$), with similar anion and cation size, but could

well characterize systems with very different relative anion and cation radii. However, in the later case, crystallization can easily occur at relatively low temperatures, due to the overall lack of chemical constraints. In fact, ionic amorphous solids are rare (although a few, e.g., $ZnCl_2$, form glasses which can be quenched from the liquid phase).

Covalent solids maximize their cohesive energy by maximizing the concentration and strength of the bonding. Covalent bonds are optimized by not only a given bond length but also a particular bond angle. The concentration of these bonds depends sensitively on the electronic structure of the constituent atoms. If we restrict discussion to bonding involving only s and p electrons, the maximum possible number of bonds per atom is four. Thus the relatively low coordination numbers of covalent solids are compatible with bond-angle constraints. Phillips (3) has pointed out that (2) must be modified when the bond angles are also fixed. Since the average number of bond angles per atom is $Z(Z - 1)/2$, the total number of constraints per atom becomes $Z^2/2$. Since each atom still has only three degrees of freedom, the constraints can all be satisfied only if

$$Z \le 6^{1/2} = 2.45. \qquad (3)$$

Thus, for example, Si ($Z = 4$) is an over-constrained covalent network, Se ($Z = 2$) is an underconstrained network, and As_2Se_3 ($Z = 2.4$) is nearly a perfectly constrained network. Consequently, we might expect amorphous silicon (a-Si) to possess large strains under all preparation conditions, but be relatively resistant to crystallization. In contrast, a-Se should be easy to prepare, but it could well exhibit intermediate-range order and it should crystallize relatively easily. Materials like a-As_2Se_3 should be optimal glass formers. In general, all of these conclusions are borne out.

There are several other issues that are important in any analysis of the structure of amorphous solids. First, it is vital to determine if the material is *inhomogeneous*. In fact, inhomogeneous alloys can often have lower energy than the homogeneous material; e.g., if homopolar bonds are stronger than the possible heteropolar bonds in a simple binary alloy or particular heteropolar bonds predominate in a multicomponent alloy, we might expect a segregation into alternating phases of different compositions. This so-called *phase segregation* can be extremely dependent upon preparation conditions, as seems to be the case for a-Si:H alloys (4). Phase separation over regions greater than 1000 Å is relatively straightforward to identify, but inhomogeneities on a smaller scale can be much more subtle.

A separate problem is that of possible *anisotropy*. For example, it is clear that all thin films have an interface region near the substrate which is very likely to be significantly different from that in the bulk. Similarly, an upper interface region must also exist, near a contact material or a free surface. Such regions occupy a much greater fraction of the volume of a film than of a bulk solid, and it is dangerous to ignore their existence. It is also very common for interface regions to possess a different composition than the bulk, or to pick up a positive or negative *space charge*. The possibility of preferred directions of growth, such as in columns perpendicular to the substrate (5), can also lead to anisotropies in many cases. Finally, the nature of the chemical bonding can result in a bulk anisotropy; e.g., a-C and its alloys are often characterized by a quasi-two-dimensional graphitic structure.

Normal Structural Bonding and Defect Configurations

In crystals, the constraints of three-dimensional periodicity ordinarily restrict the

chemical bonding to its simplest form, with two-center covalent, ionic, or coordinate bonding predominating. More exotic chemistry, such as multicenter bonds, multiple bonds, complexing, orbital expansion, etc., is much rarer in crystals than in large molecules. In contrast, amorphous solids do not have periodic constraints, and a much richer chemistry is possible (6). Thus it is useful to distinguish between (1) normal structural bonding for given constituent atoms, (2) more unusual bonding, which can characterize particular alloys, and (3) defect configurations, which appear only because of imperfect preparation conditions and/or strains during growth.

For covalent alloys, bonding ordinarily obeys the rule that each atom in columns I–IV of the Periodic Table optimally forms N bonds (where N represents the number of the appropriate column), while each atom in columns IV–VIII forms $8 - N$ bonds. The minimum-energy configuration is generally brought about by maximal bond formation, so that atoms with up to a half-filled electronic shell ($N \leq 4$) bond all of their outer electrons, even if an $s-p$ promotion is necessary. The reason for this is quantitative, arising from the facts that *two* extra bonds can be formed after the promotion and all of the hybridized bonds are stronger than pure p bonds. On the other hand, since conversion of an electron pair into a bonding–antibonding pair always results in an energy increase, each electron added after $N = 4$ reduces the number of bonds by one. However, in alloys containing atoms with both $N < 4$ and $N > 4$, coordinate bonds between lone pairs and empty orbitals can increase the average coordination.

In both amorphous and crystalline solids, the one-electron states spread from their degenerate atomic energy levels as the other atoms are brought closer. The resulting quasi-continuum of levels then forms the energy bands that characterize the density of states, $g(E)$, in the solid. Thus, we

can identify bonding, antibonding, and lone-pair bands in solids (7). Sketches of this process for a-Si ($N = 4$) and a-P ($N = 5$) are shown in Fig. 2 (8). Chalcogens ($N = 6$) are different in the sense that the highest-energy filled band is a lone-pair rather than a bonding band.

The total energy of atoms in each possible configuration can be evaluated in terms of simple parameters, using the tight-binding approximation (9). The result is that well-defined *defect* configurations can be identified, but it is clear that all other *neutral* configurations than that represented by normal structural bonding have considerably higher energy. For example, chalcogen atoms can have dangling bonds, costing a bond energy, or be overcoordinated, costing a bonding–antibonding energy loss (10). Pnictogen ($N = 5$) atoms can also have dangling bonds with a similar energy increase or be overcoordinated, but with a much larger energy cost due to the necessity of an $s-p$ promotion (11). Tathogen ($N = 4$) atoms cannot overcoordinate, but can have either dangling bonds or a twofold coordination without any hybridization (12). Most of these defects can be identified by an electron spin resonance (ESR) experiment, which observes the presence of unpaired spins. Of the defects enumerated, only a twofold-coordinated tathogen does not possess an unpaired spin when neutral.

Classical Theory of Amorphous Semiconductors

The classical theory of amorphous semiconductors is due primarily to Mott (13) and Cohen *et al.* (14). Mott proposed that after the atomic energy levels spread into bands in an amorphous solid, a critical density of states exists above which all states exhibit a finite mobility for the transport of free carriers but below which all states can be considered to be essentially localized. This critical density defines what has come
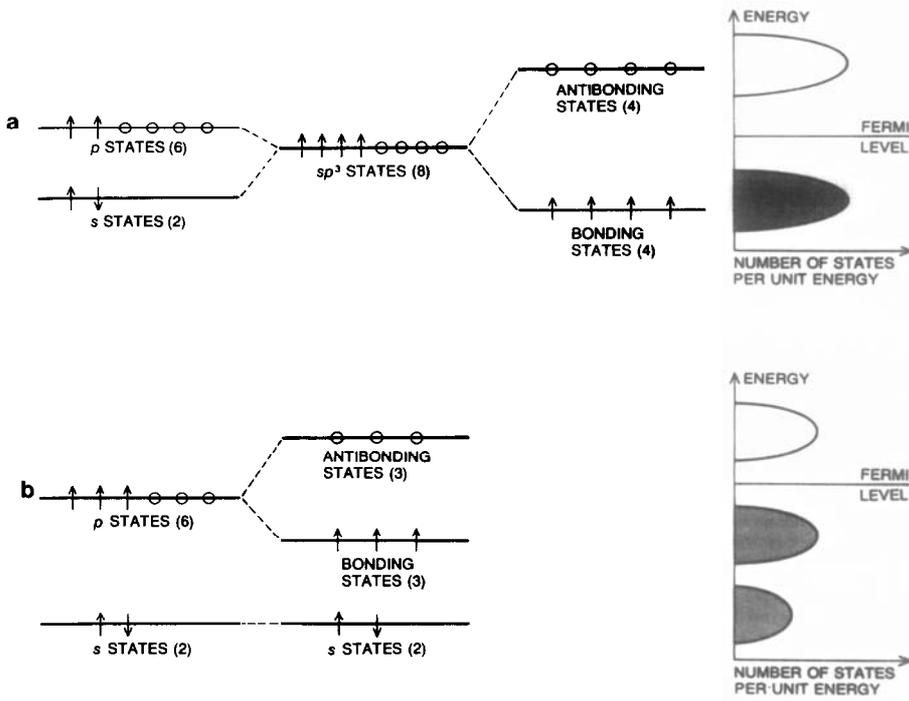
FIG. 2. (a) Electronic structure of silicon. The "bond structure" for a tathogen atom in its ground-state configuration; the "bond structure" of a small molecule is shown on the left, and the "band structure" of a solid is shown on the right. (b) A similar sketch for a pnictogen atom in its ground-state configuration. (From Adler, Ref. (8)).

to be called *mobility edges*, in analogy to the band edges in crystals. The concept of mobility edges has never been put on a firm theoretical basis, but its operational basis appears to be satisfactory (15).

Cohen *et al.* (14) assumed the existence of mobility edges and further suggested that for particularly disordered solids the valence and conduction bands could overlap in the gap center, yielding a finite density of states at the Fermi energy, $g(\epsilon_F)$. However, the material is still a semiconductor rather than a metal, provided $g(\epsilon_F)$ is less than the critical density of states defining a mobility edge. Cohen *et al.* also tacitly assumed that all atoms in the solid exhibit only normal structural bonding.

The model of Cohen *et al.* suggests that two types of amorphous semiconductors exist, depending on the magnitude of $g(\epsilon_F)$.

If $g(\epsilon_F)$ is large, say, of the order of 10^{18} cm^{-3} eV^{-1} or more, the Fermi energy should be strongly pinned. Such materials should exhibit at most a very small field effect, intrinsic conduction, and a large spin density, among other characteristics (16). Alternatively, if $g(\epsilon_F)$ is of the order of 10^{15} cm^{-3} eV^{-1}, we should expect a large field effect, extrinsic conduction, and a small spin density. *A priori* prediction would suggest that multicomponent glasses, such as the materials Ovshinsky (17) had been investigating for switching applications, should fall in the former category, while simple materials like a-Si and a-Se should fall into the latter.

Unfortunately, the experimental data did not bear out these predictions. In fact, pure a-Si films have *none* of the predicted characteristics. In sharp contrast, however, a-

Si : H alloys behave in just the manner expected from the previous analysis. The obvious conclusion is that $g(\epsilon_F)$ is large for pure a-Si but not for a-Si : H alloys. However, we must explain the origin of this strange result.

The experimental data on amorphous chalcogenide alloys present even greater difficulties. In general, all of these materials from pure a-Se through multicomponent glasses like a-$Te_{40}As_{35}Si_{15}Ge_7P_3$ exhibit negligible field effects and only intrinsic conduction, but have no observable unpaired spins at equilibrium. This suggests that ϵ_F is strongly pinned without a significant $g(\epsilon_F)$, an apparent self-contradiction. Clearly, a great deal needs to be explained.

Amorphous Silicon Alloys

The key to understanding a-Si and its related alloys is the fact that it forms an overconstrained network. Strains introduced during deposition lead to significant concentrations of defect centers, and it is these which yield the large values of $g(\epsilon_F)$ that characterize pure a-Si films. As previously indicated, the simplest defects that might be expected are dangling bonds and twofold-coordinated Si atoms. We use a notation A_z^q, where A represents the atom under consideration (T for tathogen, P for pnictogen, and C for chalcogen), z represents the local coordination number, and q represents the charge state. Thus the neutral defect centers expected in a-Si are T_3^0 and T_2^0. Tight-binding calculations (*11*) suggest that T_3^0 defects yield two localized states in the gap, one filled and one empty, while T_2^0 defects yield up to four states in the gap, two filled and two empty. In addition, all T_3^0 centers contain an unpaired spin, which yields an ESR signal. If the defect concentrations are large, these states overlap and spread into bands, ultimately resulting in a $g(\epsilon_F)$ sufficiently large to pin the Fermi energy. This explains the data on pure a-Si.

When a-Si is hydrogenated, the average coordination number decreases by three times the hydrogen concentration. Thus a-Si : H alloys are subject to fewer strains during deposition. More important, hydrogen is a small atom which can diffuse quickly through the material and is capable of forming an extra bond with a T_3^0 center. Since the Si–H bond is about 40% stronger than the Si–Si bond, formation of Si–H bonds effectively removes the defect-related states from the gap. Thus hydrogen both eliminates the ESR signal and unpins ϵ_F, as observed. Similar results are found when a-Si films are fluorinated (*18*).

When defects are present, the traditional analysis of transport experiments must be modified. This problem also exists in imperfect crystalline semiconductors, and is due to the invalidity of the one-electron approximation for localized states. As discussed previously, the one-electron approximation neglects the possibility that two electrons can correlate their motion to minimize their mutual repulsion. Consequently, the total energy is overestimated by a term proportional to the repulsion between two electrons simultaneously located on the same atomic site, a term usually called U (*19*). In extended states, screening of the coulomb interaction by mobile electrons reduces the value of U sufficiently so that electronic correlations can be neglected without serious error; however, screening is not so effective in localized states, and a different approach is essential.

Consider a T_3^0 center. When a Si atom forms only three bonds, the eightfold-degenerate sp^3 levels are split such that three filled bonding orbitals have low energy, three empty antibonding orbitals have high energy, and two nonbonding levels lie in between, one filled and one empty. The filled level appears on a one-electron density-of-states diagram at the energy of attraction of the nonbonding electron for the T_3^+ center it would leave behind when io-

nized. If no electron were present on that T_3^+ center, the level would be doubly degenerate, since either a spin-up or a spin-down nonbonding electron can be placed on the center. However, if *two* nonbonding electrons were to be placed on the center, converting it into T_3^-, there would be an additional repulsion between the two localized negative charges, the U term just discussed. Thus, if and only if one of the two states in the gap is occupied, the other state increases its energy by U. In this way, we go beyond the one-electron approximation and take correlations into account. Ordinary Fermi statistics must be modified, but the final result is straightforward (*20*).

Amorphous Chalcogenide Alloys

The key to an understanding of amorphous chalcogenide alloys is how a pinned ϵ_F can be consistent with the lack of observation of unpaired spins. Anderson (*21*) suggested that this difficulty could be resolved if U were negative rather than positive. In such an unusual situation, is which two electrons localized on the same center effectively *attract* each other, occupation of the orbital by one electron would move the second energy level below the first. Any other unpaired electron in a nonbonding orbital could then lower its energy by moving on the same site as the first, leading to a spin pairing. In fact, if $U < 0$, all centers will be either doubly occupied or unoccupied, independent of the concentration of electrons in the defect levels. Thus no unpaired spins are present at equilibrium. But, in addition, any pair of electrons added to the material will preferentially go to the *same* center, converting an unoccupied center to a doubly occupied one. Since the additional electrons always enter with the same energy, ϵ_F is strongly pinned (*22*).

Although Anderson's suggestion resolves the difficulty of how ϵ_F can be pinned without the creation of a significant concentra-

tion of unpaired spins, it actually replaces it with *two* new problems: (1) Why would an underconstrained network such as a-Se have a sufficiently large defect concentration to pin ϵ_F even if $U < 0$? (2) How can two localized electrons mutually attract? The key to understanding both of these lies in the chemical nature of the chalcogen atoms (*10*). The answer to the first question is that a defect pair with very low creation energy exists which is unique to chalcogenides. This pair consists of a positively charged, overcoordinated chalcogen ion, C_3^+, together with a negatively charged dangling bond, C_1^-, P_2^-, or T_3^-. Such a pair, called a *valence alternation pair* (VAP) by Kastner *et al.* (*10*), has a low creation energy because the total number of covalent bonds is the same as in the ground state. This arises from the fact that a positively charged chalcogen is isoelectronic with a neutral pnictogen, and thus it forms three covalent bonds in its ground state. The corresponding negative ion is also optimally bonded, so that neither center has any unpaired spins. The creation energy is primarily due to the additional repulsion from the extra electron on the negatively charged ion; this can be estimated to be about 0.5 eV. Thus the Law of Mass Action indicates that the order of 10^{19} cm^{-3} VAPs are frozen in at the glass transition temperature (i.e., the softening point).

The effective attraction between electrons on VAPs arises from the fact that a C_3^+ center can convert to a C_1^-, P_2^-, or T_3^- center by a simple bond breaking. For example, if extra electrons are injected into a chalcogenide alloy containing a concentration of VAPs of 10^{19} cm^{-3}, then the first electron is trapped in the high-energy antibonding orbital on a C_3^+ center, converting it to a C_3^0. If the alloy were an ordinary semiconductor, succeeding electrons would also be trapped on the same C_3^+ centers. However, in chalcogenides, the second electron has a much lower energy level when it transfers to any

one of the three nearest neighbors of the C_3^0 center. Upon breaking the bond between the C_3^0 center and that neighbor, the C_3^0 center becomes a ground-state C_2^0 atom while the neighbor becomes a negatively charged dangling bond (C_1^-, P_2^-, or T_3^-). Thus the two extra electrons form a lone pair on the latter center, and the added repulsion is more than overcome by the loss of two antibonding electrons. The net reaction is, e.g.,

$$C_3^+ + 2e^- \rightarrow P_2^-. \qquad (4)$$
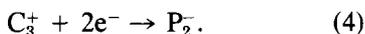
Since the second electron has lower energy than the first, the effective value of U is negative; since the two electrons are always spin-paired (as a lone pair) on the negative center, there is no ESR signal at equilibrium; since all pairs of excess electrons enter with the same total energy, ϵ_F is pinned; finally, since pnictogens can overcoordinate only after an s–p promotion and tathogens cannot overcoordinate at all (unless d hybridization occurs), large VAP densities are unique to chalcogenides.

Amorphous Silicon Alloys Revisited

After the previous detailed analysis of defect centers in chalcogenides, it is reasonable to ask for the sign of the effective correlation energy for defects in a-Si alloys. It is clear that T_2 centers have a positive correlation energy (23). Unfortunately, the situation is far from clear with regard to the dangling bond, T_3 (24). The reaction

$$2T_3^0 \rightarrow T_3^+ + T_3^- \qquad (5)$$
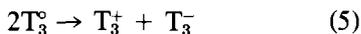
preserves the total number of bonds but eliminates one s–p hybridization (on the T_3^- center); thus it could well be exothermic. Nevertheless, a-Si alloys clearly exhibit an ESR signal which is attributed to T_3^0 centers (25). This suggests one of three possibilities: (1) the correlation energy of T_3 centers is positive (25); (2) the correlation energy of isolated T_3 centers is positive, yielding the observed spins; however, intimate charged

T_3^+–T_3^- centers are stabilized by the additional coulomb attraction between spatially close oppositely charged centers (26); or (3) the effective correlation energy is indeed negative; nevertheless, unpaired spins can be frozen in metastably (27). The last possibility is worth some amplification. Note that T_3^+ and T_3^- are both the lowest-energy configuration for their electronic structure. However, although both centers have the same coordination number, the bond angles are very different: T_3^+ should exhibit predominately sp^2 bonding with a bond angle near 120°, while T_3^- should exhibit primarily p bonding with a bond angle in the range 90–100°. Thus, although the two neutral centers can interconvert by a local rearrangement, it is extremely likely that such an interconversion would require the overcoming of a potential barrier. In this case, thermal equilibrium would be attained only at sufficiently high temperature. At lower temperatures, a metastable spin density would be frozen in.

There is actually a great deal of evidence in favor of this point of view. When a-Si:H films are exposed to intense light, there is a metastable change in ϵ_F (28) and the spin density increases (29). A field-induced excess conductivity has been observed in such films upon quenching (30) and a similar change in ϵ_F has been observed (31). In all cases, the annealing kinetics are similar, suggesting a process with an activation energy in the range 0.9–1.5 eV. Recent transient experiments have also been interpreted in terms of the same model (32).

Transient Effects

The previous discussion focuses on a potential problem which should also be important in chalcogenides. In any transient experiment in a system containing negatively correlated defects, we might expect metastable trapping of excess free carriers by the charged centers. In fact, such metasta-

ble effects have been observed in glasses in the Te–As system (33). Transient field effects, unusual photoconductivity behavior, photo-induced absorption, photo-luminescence fatigue, and even threshold switching effects now appear to be affected by the presence of metastable neutral centers. Whenever a potential barrier exists between the interconvertible neutral centers of a negatively correlated defect, we must immediately identify two regimes of time and temperature. For large times compared to $\nu_0^{-1} \exp(W/kT)$, where ν_0 is a typical phonon frequency ($\sim 10^{12}$ sec^{-1}) and W is the height of the barrier, equilibrium is attained and we can use the Fermi–Dirac distribution function appropriate to a negative effective U. In contrast, for short times compared to $\nu_0^{-1} \exp(W/kT)$, the interconversion is frozen out and the defect centers have a positive U. This presents still another complication in data analysis, but neglect of these effects can lead to erroneous conclusions.

Conclusions

Perhaps the most striking experimental result thus far obtained in studies of the covalent amorphous semiconductors is the sharp dichotomy between the properties of a-Si alloys and the chalcogenides. Although many questions still remain, from our present viewpoint the origin of the differences is: (1) In a-Si alloys, all defects have a large creation energy; this directly stems from the fact that four sp^3 bonds represent the optimal configuration involving only s and p electrons. Thermodynamically, the total defect concentration should be quite small. In chalcogenides, a very low energy defect exists, a VAP. Consequently, the Law of Mass Action requires a minimum defect density in the range 10^{18}–10^{20} cm^{-3}. (2) On the other hand, a-Si alloys ordinarily form an overconstrained network; thus strain-induced defects are introduced upon deposition. The incorporation of hydrogen or fluorine sharply reduces the concentration of these defects both by lowering the average coordination number and by saturating the dangling bonds and perhaps even lower-coordinated centers. In sharp contrast, chalcogenides are not generally overconstrained and nonthermodynamic defects exist only under extremely rapid quenching conditions. (3) In chalcogenides, one type of defect center usually predominates, the VAP with the minimum creation energy. In a-Si alloys, several types of defect can simultaneously be present. Possibilities include T_2^0, T_3^+–T_3^-, T_2^+–T_3^-, and T_3^0. The T_3^0 center can have at least two different structures. (4) In chalcogenides, ϵ_F is ordinarily pinned by the negative effective U; in silicon alloys, ϵ_F need not be pinned, particularly if the defect concentration is low. (5) Transient effects can be characterized by different effective values of U for both types of material; the actual U to be used depends on both the temperature and the time scale of the experiment.

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