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ORIGIN OF THE PHOTO-INDUCED CHANGES IN HYDROGENATED AMORPHOUS SILICON*

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Summary

The electronic properties of hydrogenated amorphous silicon films are discussed in detail. Particular attention is paid to the changes induced by photogeneration of excess free carriers. Previous models which have been proposed to account for such effects are classified and criticized. An alternative explanation, which is based on the unique electronic structure of hydrogenated amorphous silicon, is proposed and analyzed. In this model, no new defects are created by the light, but rather the photo-induced effects follow from a metastable trapping of the excess free carriers at charged spinless defects which are present at equilibrium.

1. Introduction

Our overall understanding of the physics of hydrogenated amorphous silicon (a-Si:H) has increased steadily over the past few years, but many problems remain. Different samples exhibit diverse electronic properties, and even different measurements on similarly prepared samples often appear to yield inconsistent results. The major unresolved problems are (1) the nature of the traps and recombination centers, (2) the mechanism for free-carrier transport, including the magnitude of the electron and hole mobilities, (3) the mechanism for doping and the effect of doping on the electronic structure and (4) the origin of the photo-induced changes which are observed even in high quality material. In this paper, I shall attempt to summarize the present situation and propose a new model which is capable of explaining the vast majority of currently available data. In Section 2, the properties of amorphous silicon-based alloys are analyzed in terms of our present

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viewpoint. Particular attention is paid to the defect structure and its effects on the density of states $g(E)$. The large body of experimental results relating to photo-induced changes is summarized in Section 3, and a critique of the models proposed to account for these changes is given in Section 4. Finally, in Section 5, an alternative model is presented and analyzed.

2. Properties of hydrogenated amorphous silicon

As Phillips [1] has pointed out, covalent amorphous solids with an average coordination number Z greater than 2.45 are overconstrained, in the sense that there are an insufficient number of degrees of freedom to optimize all the bond lengths and bond angles. Thus pure a-Si, with $Z = 4$, is highly overconstrained. Clearly, hydrogen greatly reduces the strains by lowering Z; for a-$Si_{1-x}H_x$, $Z = 4 - 3x$; consequently, even for an alloy with 30% H, $Z = 3.1$ and the network is still somewhat overconstrained. We can conclude that all a-Si:H films necessarily contain local strains which are introduced during the growth process. In most cases these strains are reflected in bond angle distortions [2], but occasionally defect configurations form. These defects are very likely to be undercoordinated silicon sites, and energetic considerations [3] suggest that both dangling bonds (T_3) and twofold-coordinated silicon atoms (T_2) are possible. It should be noted that a-Si:H films differ sharply from amorphous chalcogenide alloys in which Z is usually less than 2.45 and thus few strain-induced defects are expected. However, chalcogenides possess at least one type of defect with a relatively low creation energy ΔE resulting in the necessary existence of large concentrations of that defect which are frozen in at the glass transition temperature for thermodynamic reasons [4]. In contrast, since tetrahedral (sp^3) bonding represents the maximum possible concentration of bonds involving s and p electrons and since hydrogen cannot form more than one covalent bond, we can conclude that no defect with low ΔE exists in a-Si:H alloys [5]. Hence, the concentration of thermodynamically required defects is negligible. It is this fact that permits the growth of a-Si:H films with superior electronic properties. However, the facts that the defects in a-Si:H are induced to relieve strains during the deposition process and that more than at least two types of defect configuration are possible lead to the conclusions that the quality of each film is very sensitive to the preparation conditions and that the relative concentrations of the defects present cannot be estimated from the law of mass action [6].

It is clearly of great importance to identify both the nature and the concentration of defects present in a-Si:H films. The many techniques currently employed for gap state spectroscopy do not directly probe the origin of the localized states detected, although some evidence is provided by their excitation energy. In addition, most of these techniques, *e.g.* field effect, transient photoconductivity and capacitance–voltage measurements, investigate surface or interface regions in which the structure of the film is

likely to be significantly different from that of the bulk, and even some studies which employ sandwich geometries, *e.g.* time-of-flight and reverse-recovery experiments, can be plagued by displacement current effects [7]. In addition, the importance of electronic correlations, to be discussed in detail later in this section, adds a major complication.

If a particular defect center is in a charge state in which an unpaired spin is present, the technique of electron spin resonance (ESR) is extremely useful. It can distinguish between different types of centers by measuring the g value and the linewidth ΔH of the signal and also yields the total concentration of each center. Light-induced electron spin resonance (LESR) experiments can be used to probe the nature and concentration of defects which are spinless at equilibrium [8], although a rapid relaxation time for the photogenerated spins could render them invisible within this technique. To date, four different centers with unpaired spins have been observed in apparently pure a-Si:H films [9]. The predominant line in undoped films is one for which $g = 2.0055$ and $\Delta H = 7$ G, a center usually identified with a neutral dangling bond, T_3^0, because of its similarity to the ESR signal near c-Si–a-SiO_2 interfaces [10] (where c-Si denotes crystalline silicon). In addition, two lines observable in LESR in undoped films are exposed at equilibrium by n-type or p-type doping. When the Fermi energy E_F is increased, a line with $g = 2.004$ and $\Delta H = 6$ G grows in intensity, while a decrease in E_F uncovers a line with $g = 2.01$ and $\Delta H \approx 20$ G. These lines have been associated with electrons in the conduction band tail (T_4^-) and holes in the valence band tail (T_4^+) [8], negatively and positively charged weak bonds [11], or T_2^- and T_2^+ centers [6]. There is also some evidence for a line with $g = 2.0026$, independent of E_F, which might originate from a paramagnetic impurity [9].

In addition to defects containing unpaired spins, spinless centers can also exist and contribute to the density of localized states. In fact, there is a great deal of evidence for their existence in a-Si:H films [6]. The most likely intrinsic spinless defects are T_3^+–T_3^- pairs and T_2^0 centers. There are theoretical reasons for the presence of both in a-Si:H [12]. T_2 centers are twice as effective as T_3 centers in lowering the average coordination of the network, they do not require the s–p promotion energy to form, and they can account for the $g = 2.004$ and $g = 2.01$ ESR lines in a natural way. Recent calculations on the Si_2H_4 molecule clearly show the relative stability of T_2^0 compared with T_3^0 centers in an Si–H compound [13].

For the case of the T_3 defects, the possible existence of T_3^+–T_3^- pairs depends upon the sign of the effective correlation energy U_{eff} of the center [14]. In the absence of atomic relaxations, the correlation energy U of a defect center D is defined by the chemical reaction [15]

$$2D^0 + U \rightarrow D^+ + D^- \qquad (1)$$

U represents the additional electrostatic repulsion between two electrons with antiparallel spins simultaneously present in the same orbital state; it is clear that U is always positive and is larger for more localized orbitals. When

atomic relaxations around the charged centers are taken into account the value of U must be renormalized, resulting in an effective value U_{eff} defined by the reaction

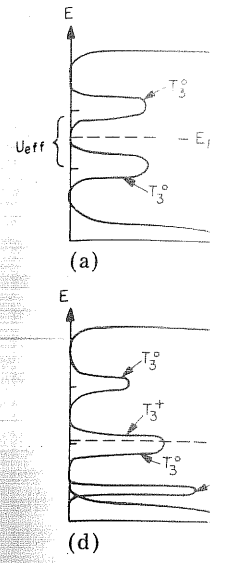
$$2D^0 + U_{\text{eff}} \rightarrow (D^+)_r + (D^-)_r \qquad (2)$$

where $(D^{\pm})_r$ represent the fully relaxed $D^{\pm}$ centers. Since relaxations lower the energies of both the D^+ and the D^- centers, U_{eff} must be lower than U. When U_{eff} is negative, the ground state of the defect is a D^+–D^- pair [16].

Tight-binding estimates [17] suggest that U_{eff} could indeed be negative for T_3 centers in a-Si:H. This possibility arises from the fact that an Si^+ ion is isoelectronic with aluminum, which optimally forms three sp^2 bonds, while an Si^- ion is isoelectronic with phosphorus, which optimally forms three p bonds. Thus both T_3^+ and T_3^- centers represent normal structural bonding rather than defect configurations. However, complete relaxation would require significant atomic motion, since the optimal bond angle for sp^2 bonding is 120° and for primarily p bonding is about 95°, both far removed from the tetrahedral 109.5° bond angles. Recalling that a-Si:H films are overconstrained, it is very likely that complete relaxation around both T_3^+ and T_3^- centers takes place in all cases. One possibility, which will be discussed in detail in Section 5, is that both T_3^+–T_3^- pairs and isolated T_3^0 centers are simultaneously present in a-Si:H films.

When T_3^0 centers are stable (*i.e.* $U_{\text{eff}} > 0$), they can be expected to give rise to two bands of states in the gap of intrinsic a-Si:H films, one below E_F and one above E_F. These two bands should exhibit a separation of U_{eff} between their centers, as is sketched in Fig. 1(a). The introduction of tetrahedrally bonded phosphorus (P_4) would be expected to create donor-like states near the bottom of the conduction band, just like in c-Si:P. These would form P_4^+–T_3^- pairs at equilibrium, increasing E_F into the upper band and effectively shifting states from the lower to the upper T_3 bands [18], as indicated in Fig. 1(b). At heavy doping levels, E_F can move into the P_4 band, as shown in Fig. 1(c). The reverse occurs when tetrahedrally bonded boron (B_4) is introduced, as indicated in Figs. 1(d) and 1(e). All these sketches ignore states resulting from the possible presence of threefold-coordinated phosphorus (P_3^0) and boron (B_3^0) centers. Such centers would be expected to result in an increase in the density of localized gap states, but P_3^0 centers should yield only filled states below E_F and B_3^0 centers should yield only empty states above E_F, so that these centers are ordinarily electrically inactive.

If $U_{\text{eff}} < 0$, E_F is pinned to the extent of the concentration of T_3 centers [19]. However, once the concentration of either P_4 or B_4 centers exceeds that of the T_3 centers, E_F begins to move significantly as shown in Fig. 2. It should be noted that Figs. 1 and 2 explicitly take into account the necessary complications which arise whenever electronic correlations are important, whatever the sign of U_{eff}. Whenever the magnitude of U_{eff} is finite, the effective density of states depends on the state of occupation [15]. Thus as E_F moves, $g(E)$ necessarily changes. Furthermore, each state of



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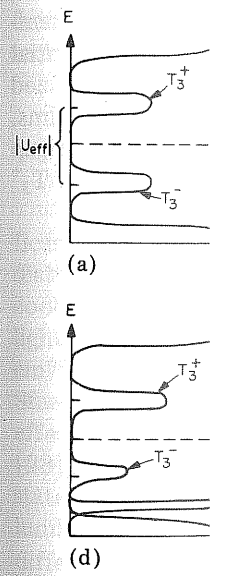

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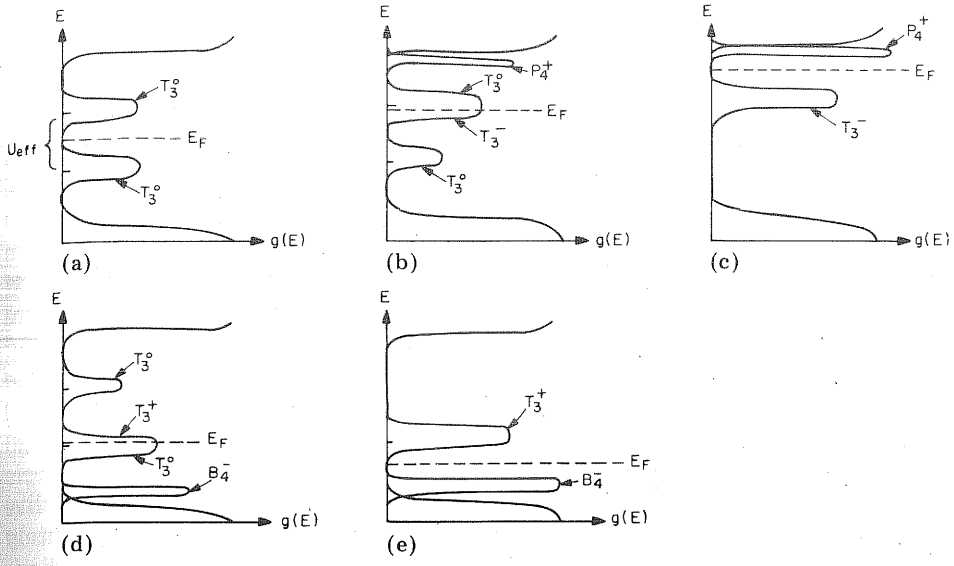

Fig. 1. Effective one-electron density of states for a tetrahedrally bonded amorphous semiconductor with dangling bond defects characterized by $U_{eff} > 0$: (a) undoped sample; (b) moderately phosphorus-doped sample; (c) heavily phosphorus-doped sample; (d) moderately boron-doped sample; (e) heavily boron-doped sample. The defect bands are labeled by their state when filled if they are located below E_F and when empty if they are located above E_F.

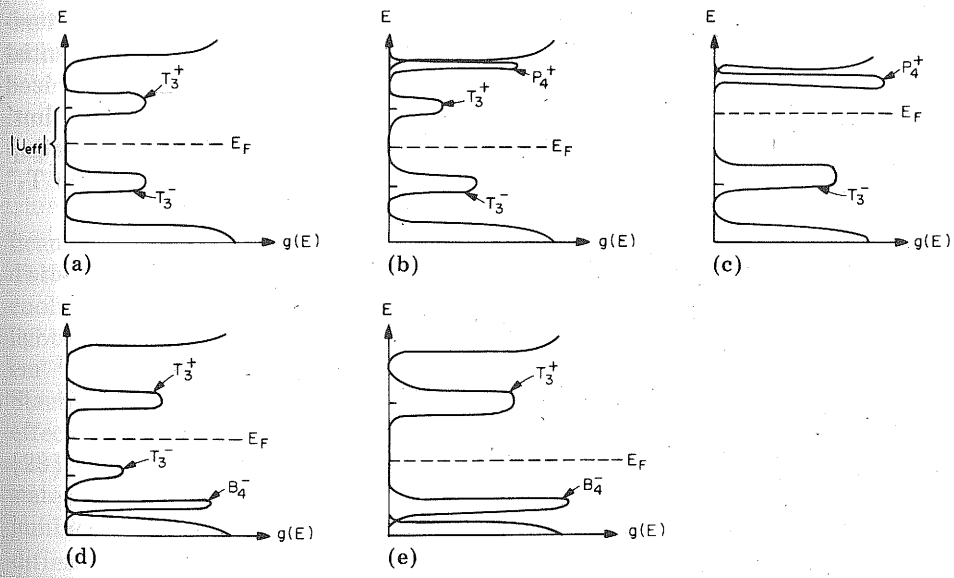

Fig. 2. Effective one-electron density of states for a tetrahedrally bonded amorphous semiconductor with well-separated dangling bond defects characterized by $U_{eff} < 0$: (a) undoped sample; (b) moderately phosphorus-doped sample; (c) heavily phosphorus-doped sample; (d) moderately boron-doped sample; (e) heavily boron-doped sample. The notation is the same as in Fig. 1.

excitation of the material has a different $g(E)$, an effect which must not be neglected in the analysis of transient experiments. For example, an observed increase in $g(E)$ in a given energy range is not necessarily due to the creation of new defects, but could result from correlation-induced shifts of weight between the defect bands. Let us consider a moderately phosphorus-doped a-Si:H alloy. If $U_{\text{eff}} > 0$, the equilibrium situation is as sketched in Fig. 1(b). Photogenerated holes will then be trapped at T_3^- centers just below E_F. This will effectively build up the density of T_3^0 states just below midgap, because of the decrease in the concentration of doubly occupied (T_3^-) centers. If $U_{\text{eff}} < 0$, the equilibrium situation is that of Fig. 2(c). Photogenerated holes are trapped at T_3^- centers well below E_F, resulting in a build-up of T_3^0 centers closer to the midgap region. The exact location in energy of these states depends on the extent of the accompanying atomic relaxations and thus on the time scale of the observations. Clearly the analysis entails a high degree of complexity.

An additional consequence of a negative value of U_{eff} is the possibility of spatial correlations between the T_3^+ and T_3^- centers [6]. Since oppositely charged centers which are closely separated have lower energy than those which are farther apart, we might expect a preponderance of the former. In fact, the law of mass action suggests that the concentration of T_3^+–T_3^- pairs separated by a distance R is given by

$$[T_3^+\text{–}T_3^-(R)] = [T_3^+\text{–}T_3^-(\infty)] \exp(e^2/2\epsilon R k T_d) \qquad (3)$$

where $[T_3^+\text{–}T_3^-(\infty)]$ is the concentration of such pairs at large separations, ϵ is the effective dielectric constant and T_d is the effective deposition temperature. The resulting density of states then takes the form of exponential distributions of ionized donor-like (T_3^+) states above E_F and ionized acceptor-like (T_3^-) states below E_F, as shown in Fig. 3 for undoped films. In such a case, E_F is no longer pinned but can be swept through the gap from the minimum of the T_3^- distribution to the maximum of the T_3^+

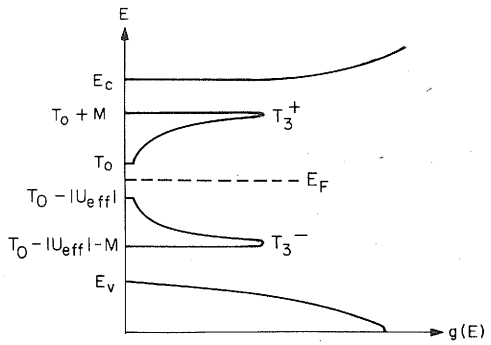

Fig. 3. Effective one-electron density of states for a tetrahedrally bonded amorphous semiconductor containing a distribution of spatially correlated dangling bond defects with $U_{\text{eff}} < 0$. T_0 represents the energy of the non-bonded electron on a neutral dangling bond, and M is the electrostatic attraction between a T_3^+ center and a T_3^- center located on nearest-neighbor sites.

distribution. Even if $U_{eff} > 0$ for isolated T_3^0 centers, T_3^+–T_3^- pairs could be stabilized by the mutual electrostatic attraction. If such were the case, the two exponential distributions in Fig. 3 would overlap in the midgap region (where their densities are relatively low).

Whatever their nature, the localized states in the gap of a-Si:H alloys act as traps and recombination centers, which limit the drift mobility, diffusion length and lifetime of photogenerated electrons and holes. However, the transport properties of these carriers also depend on the nature of their propagation between trapping events. This could be via hopping among localized states, diffusion in a concentration gradient, or ordinary band-like transport in the applied electric field. These processes can be distinguished by the magnitude and temperature dependence of the carrier mobility [20]. Recent work [21] has indicated that both electrons and holes propagate in a band-like manner in high quality a-Si alloys, and in fact the band mobility of electrons is of the same order of magnitude as in c-Si. Previous lower estimates of the carrier mobility are very likely to have been erroneous because of large displacement current effects [7]. We can conclude that the similar nearest-neighbor and next-nearest-neighbor environments in a-Si:H and c-Si preserve the essential features of the valence and conduction band structure. The larger band gap in the amorphous alloys is due primarily to the fact that the Si—H bonding is stronger than homopolar Si—Si bonding [22]. It now appears that the major difference between c-Si and a-Si:H in so far as transport is concerned is the greater concentration of traps and recombination centers in the amorphous films. Since these traps originate from strain-induced defects, there is hope that improved preparation techniques can ultimately yield semiconductor grade a-Si films.

3. Summary of photo-induced changes in hydrogenated amorphous silicon

Staebler and Wronski [23] observed that application of light can significantly affect the electronic properties of a-Si:H films. They were able to distinguish between two states, a fully annealed state attained by slowly cooling the material from approximately 500 K in the dark (state A) and a light-soaked state attained after the application of the order of 10^{25} photons cm^{-2} to the material at room temperature (state B). Since the work of Staebler and Wronski, there have been many investigations of photo-induced effects in a-Si:H films. Changes have been observed in the photoconductivity [23], carrier diffusion length [24], unpaired spin density [25], density of states in the gap [26, 27], absorption coefficient near midgap [28], photoluminescence [29] and IR transmission [30]. A summary of the major differences between states A and B is given in Table 1. A significant contribution is the recent work of Tanielian [31], who attributed the large changes in conductivity to variations ΔE_F in the Fermi energy. Tanielian showed that ΔE_F is a function of the Fermi energy E_{Fo} in state A, as shown in Fig. 4. In general, light induces E_F to move toward midgap, the effect being most

TABLE 1

Differences between A and B states

Property	*Change upon transition A → B*	*Remarks*
σ	Decreases (except when E_{Fo} near midgap or near mobility edges)	Due to ΔE_F; ΔE_F a sensitive function of E_{Fo}
σ_{ph}	Decreases	Bimolecular → monomolecular for ν-type material
L_p	Decreases	$\Delta\mu_H \to 0$ implies τ decreases
N_s	Increases	$\Delta N_s \approx 10^{17}$ cm^{-3}; separation greater than 10 Å (g = 2.0055)
$g(E_F)$	Increases	
$g(E)$	Increases near midgap and below	
α	Increases near 1.1 eV	$\Delta E_{opt} \approx 0$
Photoluminescence	1.2 eV peak decreases, 0.8 eV peak increases	

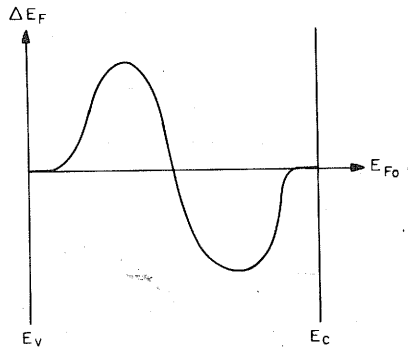

Fig. 4. Photo-induced change ΔE_F in Fermi energy in a-Si:H films as a function of the original position of the Fermi energy E_{Fo} in state A.

pronounced for moderate doping levels but vanishing for heavy doping. Dersch *et al.* [25] found a light-induced increase in the unpaired spin concentration of undoped a-Si:H samples by a factor of about 2 - 4, depending on the level of illumination. Only the T_3^0 spins (g = 2.0055) were observed and no exchange narrowing was noted, indicating that the photo-induced spins are at least 10 Å apart. The new spins do not appear to be due to ΔE_F, since the films were undoped. Morigaki *et al.* [32] obtained similar results, finding an increase in unpaired spin concentration to about 10^{17} cm^{-3} after exposure with an argon laser. In each case, the light-induced increase in N_s anneals away in the same way as does ΔE_F.

The characteristics of the A → B transition are summarized in Table 2. State B can be induced by any process which creates free carriers, including irradiation with X-rays [33] and injection from electrodes [34]. The transition occurs upon recombination of the excess free carriers [34, 35] which is,

TABLE 2

Characteristics of A → B transition

Induced by photons ($\hbar\omega > 1.6$ eV), X-rays, electrons, ions or free-carrier injection
Occurs upon recombination of excess carriers
ΔN_s has a rate of creation of about 10^{-8} spins per photon initially and saturates at about 10^{17} cm^{-3}
Induced at any temperature (4 - 400 K)

of course, when energy from the incident light is transferred to the ion cores. We can conclude that any new defects created by the recombination of free carriers can be induced by 1.6 eV or less. State B can apparently be induced at any temperature from 4 K upward until the rate of the reverse B → A transition precludes its observation [36]. Finally, it should be noted that the transition is a relatively inefficient process; *e.g.* the increase of N_s takes place at a rate of about 10^{-8} spins per absorbed photon prior to saturation [37]. This suggests that state B can be induced via a very minor recombination process and could even be coupled to an unintentional impurity such as oxygen, nitrogen, carbon or chlorine, which are always present in a-Si:H films in low concentrations.

Finally, the characteristics of the reverse B → A transition are summarized in Table 3. The most significant result is that state A can be completely recovered by annealing (although not by the application of IR light). The process is temperature activated; there is a great deal of uncertainty in estimating the activation energy E_a from an Arrhenius plot over a narrow temperature range, and a range of values for E_a between 0.9 and 1.5 eV have been reported. It should be noted that the infinite temperature extrapolation of such an Arrhenius plot yields the attempt frequency ν_0 for the transition. The wide range of reported values of E_a suggests that ν_0 can be anywhere between 10^8 and 10^{15} s^{-1}. If we assume that ν_0 is a typical atomic vibrational frequency (about 10^{12} s^{-1}), then the observed annealing times in the 150 - 220 °C range indicate $E_a \approx 1.2$ eV. Such a situation is consistent with a model in which the B → A transition is driven by excitation over a potential barrier of approximately 1.2 eV [38]. In any event, we can conclude that B is a metastable state induced by recombination of a small fraction of the

TABLE 3

Characteristics of B → A transition

Induced by temperature $T > 400$ K
Energy of activated process $E_a \approx 0.9$ - 1.5 eV
Not induced by IR light
Appears to be completely reversible

excess free carriers. The apparent reversibility of the transition also suggests that the photo-induced defects are distinguishable from the native defects which are also present in state A (since only the photo-induced defects anneal away). However, the ESR results indicate that *both* are T_3^0 centers.

Many of the complex results obtained on solar cells reflect much simpler materials properties. For example, the faster rate of solar cell deterioration under open-circuit as compared with short-circuit conditions arises from the fact that the A → B transition occurs upon recombination. The greater recombination rate in the absence of any current maximizes the rate of conversion from state A to state B; when a current flows, some of the photogenerated carriers are collected, retarding the A → B transition rate. The light-induced shift of E_F toward midgap (Fig. 4) clearly leads to a collapse of the internal field in most solar cell geometries. In a-Si:H cells, the resulting reduction in the drift component of the photocurrent leads to decreases in both J_{sc} and the fill factor, as observed. In connection with this it should be noted that the existence of accumulation regions near free surfaces in a-Si:H [39] indicates why photo-induced changes are often attributed to surface effects [4]. As is evident from Fig. 4, the large light-induced decrease of E_F in the accumulation region relative to the small change in the intrinsic bulk simulates a surface effect.

4. Models for photo-induced changes in hydrogenated amorphous silicon

Although many models have been proposed to account for the A → B transition, they generally fall into two main classes: (1) defect creation models [25, 41] and (2) electron trapping models [30, 42]. In the former, light results in the generation of new defects which act as additional traps and recombination centers. These new defects lower the carrier diffusion lengths, the photoconductivity and the intensity of the 1.2 eV luminescence, they increase $g(E)$ and α near midgap, and they increase N_s. With a specific model for the T_3^0 defect levels, Tanielian *et al.* [41] were able qualitatively to understand Fig. 3 in detail. Nevertheless, there are problems with such models [6]. Since there is strong evidence that there are more unpaired spins in state B than in state A, then some spin pairs must be broken in the A → B transition. This indicates that excess-carrier recombination must create two new defects. However, less than 1.6 eV is available from each recombination event, an extremely small amount of energy to create a pair of defects. In addition, the fact that the photogenerated spins are farther than 10 Å apart suggests that long diffusions must occur after the recombination process. It is difficult to conceive of a silicon atom moving more than a fraction of an interatomic spacing, even if it has a dangling bond. Unbound hydrogen atoms can diffuse rapidly, but the breaking of two Si—H bonds requires nearly 7 eV and, in any event, there is no reason why recombination events should occur near strong Si—H bonds. Other results which are difficult to explain include the large activation energy necessary for recovery of state A

and the complete reversibility of the transition. If the new defects are T_3^0 centers, which are also native defects, then why do only the photogenerated defects anneal away?

Electron trapping models attribute the light-induced changes to the existence of a metastable trap in a-Si:H films. Such models account for the recovery kinetics in a natural way, but they have difficulties in interpreting many of the other data. The ESR results show an increase in N_s only for $g = 2.0055$ with $\Delta H = 7$ G. It would be astounding if the trapped electron were not a T_3^0 center but had exactly the same g value and linewidth. In addition, these models require hole traps to exist in order to restore charge neutrality; such trapped holes must yield unpaired spins, but no new ESR signal has yet been observed which can be attributed to them. Furthermore, models that emphasize electron traps cannot account for the increase in E_F observed for moderate p doping (Fig. 4). In fact, the functional dependence of ΔE_F on E_{Fo} appears to be very symmetric around the midgap region, unlikely to be understood with a model which emphasizes only the trapping of one carrier type. Finally, there is the problem of the large activation energy for recovery; since E_a is larger than the activation energy for conduction, it is difficult to understand why more rapid equilibration does not take place via the conduction band.

Street [43] has recently made the interesting suggestion that, under photoexcitation, the quasi-Fermi levels move into the band tails, creating localized T_4^+ and T_4^- centers. If these are unstable toward dangling bond formation, *e.g.* via the process

$$T_4^- + T_4^0 \rightarrow T_3^- + T_3^0 \qquad (4)$$

then excess dangling bonds could be created metastably. However, there are several difficulties with this model. Processes such as (4) are unlikely to be exothermic, because of the loss of the bond energy upon the $T_4^0 \rightarrow T_3^0$ transition; it seems highly improbable that the decrease in energy from the $T_4^- \rightarrow T_3^-$ transition, typically less than half the gap, could overcome the loss of a bond energy of about 2.4 eV [22]. In addition, the metastable state in this model contains nearest-neighbor dangling bonds, a necessity when an Si—Si bond breaks, and this is incompatible with the experimental result that the unpaired spins in state B are separated by more than 10 Å [25].

5. Alternative model

Given the severe difficulties that plague all the current models for the origin of photo-induced changes in a-Si:H, it is useful to seek alternative explanations. In this section, I suggest a new possibility in which the unique properties of a-Si:H are invoked in a fundamental way. The essential hypotheses are (1) $U_{eff} < 0$ for the T_3 defect, provided that complete atomic relaxation can occur around both the T_3^+ and the T_3^- centers, but (2) since a-Si:H films are overconstrained such complete relaxation is often retarded,

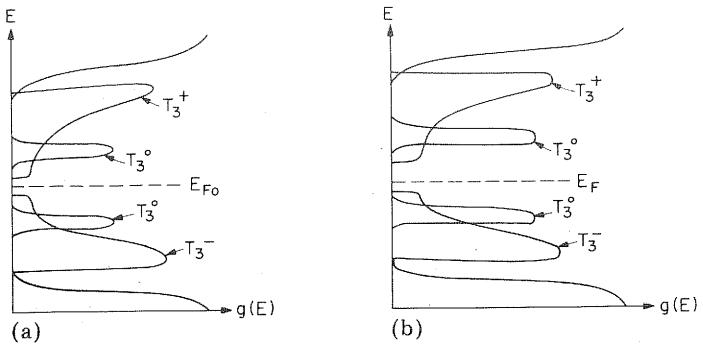

Fig. 5. Effective one-electron density of states for a-Si:H films under the assumption that dangling bond defects are characterized by $U_{\text{eff}} < 0$ if complete atomic relaxations are possible, but that such relaxations are retarded in many strained regions: (a) equilibrium state (A); (b) light-soaked state (B).

so that large concentrations of isolated T_3^0 centers are also present in all samples. There is evidence from nuclear magnetic resonance data [44] that a-Si:H films are inhomogeneous, consisting of regions with either high or low concentrations of hydrogen, and this could well be responsible for the assumed simultaneous presence of both T_3^+–T_3^- pairs and isolated T_3^0 centers. In any event, the effective one-electron density of states for such a film at equilibrium (*i.e.* in state A) is as shown in Fig. 5(a).

Upon the application of light, excess free electrons and holes are generated. The isolated T_3^0 centers can trap either electrons or holes via the processes

$$T_3^0 + e^- \rightarrow T_3^- \tag{5}$$

$$T_3^0 + h^+ \rightarrow T_3^+ \tag{6}$$

However, since these are located in relatively strained regions, the T_3^+ and T_3^- centers are unlikely to induce significant atomic relaxations and the trapped carriers remain out of equilibrium. Thus the isolated T_3^0 centers act like conventional (neutral) traps.

Spatially close T_3^+–T_3^- pairs (which because of eqn. (3) represent the vast majority of charged gap states) act as relatively shallow electron and hole traps, via the processes

$$T_3^+ + e^- \rightarrow T_3^0 \tag{7}$$

$$T_3^- + h^+ \rightarrow T_3^0 \tag{8}$$

Since these centers have states relatively near the conduction and valence band mobility edges, the trapped carriers are likely to be rereleased quickly. In contrast, widely separated T_3^+–T_3^- pairs have energies closer to the midgap region and are not likely to rerelease trapped carriers very rapidly. If dangling bonds in a-Si:H were conventional defects, the T_3^0 centers resulting after widely separated T_3^+ and T_3^- centers trap electrons and holes respec-

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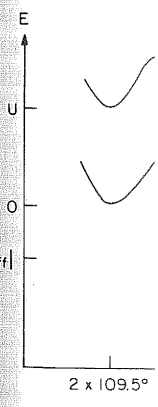

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tively would most likely trap the opposite type of carrier and thus act as recombination centers. However, another possibility exists, because of the atomic relaxations that can freely occur in relatively unstrained regions. Once either reaction (7) or reaction (8) occurs, there should be a rapid change in configuration from the 120° and approximately 95° bond angles that are optimal for T_3^+ and T_3^- centers respectively to the 109.5° bond angles appropriate for T_3^0 centers. This induces a shift in the effective density of the states from the situation sketched in Fig. 2(a) to that in Fig. 1(a). Once this shift occurs, the trapped electrons fall below E_F and the trapped holes move above E_F; *i.e.* the carriers have recombined, without any additional trapping event. In addition, because of the increase in the concentration of T_3^0 centers, a shift in the density of localized states from that sketched in Fig. 5(a) to that in Fig. 5(b) has been induced by the light. The photo-induced state, however, does not represent an equilibrium situation, since its energy can be reduced by the process

$$2T_3^0 \rightarrow T_3^+ + T_3^- \tag{9}$$

followed by the appropriate atomic relaxations. However, reaction (9) involves overcoming a potential barrier, as can be seen from Fig. 6. This sketch shows the total energies of both sides of reaction (9) as functions of a configuration coordinate q which represents two bond angle variations. The two metastable T_3^0 centers have 109.5° bond angles; only when one increases toward 120° and the other decreases to near 95° will the total energy of the T_3^+–T_3^- pair be lower than that of the two T_3^0 centers. Since two sets of bond angles must distort, the resulting potential barrier can be quite large, even 1.5 eV. The metastable state, state B, has a larger concentration of T_3^0 centers than does state A; no other ESR signal is required in either state, in accordance with the experimental results. Since the photo-

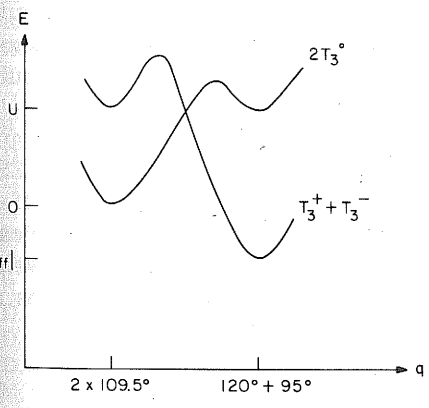

Fig. 6. Total energy as a function of a configuration coordinate q which represents a function of the two bond angles around a pair of dangling bond defects. Two charge configurations are possible for the pair, $2T_3^0$ and $T_3^+ + T_3^-$, and the energies of both are plotted. The two curves shown will interact, resulting in a potential barrier between the ground states of the possible charge configurations.

induced T_3^0 centers evolve from the more widely separated T_3^+–T_3^- pairs whose energies are near midgap, they are farther than 10 Å apart and yield no exchange narrowing, in accordance with the data of Dersch *et al.* [25]. Since the metastable centers are neutral, they are more localized in energy than the charged T_3^+–T_3^- pairs; thus they can yield an increase in $g(E)$ near midgap, as observed [41]. Only the metastable centers anneal away, since only they are located in regions which are sufficiently unstrained so that reaction (9) is exothermic. The metastable T_3^0 centers saturate because they do not represent new defects induced by the light but just arise from the repopulation of defect centers initially present.

As the films are doped with phosphorus, several effects occur. For moderate doping, the centers in the relatively unstrained regions become asymmetric, as shown in Fig. 2(b) (to which the exponential distributions resulting from spatial correlations must be added). A reversed asymmetry involving the dangling bonds in the more strained regions also occurs, resulting in a contribution to $g(E)$ of the form sketched in Fig. 1(b). The trapping of photogenerated carriers by widely separated T_3^+–T_3^- pairs again induces a metastable increase in the latter contribution; since some of these states must have a T_3^- configuration in phosphorus-doped samples (see Fig. 1(b)), E_F must decrease to maintain charge neutrality. However, for heavy phosphorus doping, no T_3^+ centers exist in either the strained or the unstrained regions (see Figs. 1(c) and 2(c)) and the entire effect disappears, as observed [31]. Similar effects occur with boron doping.

It is clear that this model accounts for many complex experimental results in a relatively straightforward manner. It is consistent with the unusual electronic structure of a-Si:H alloys and can account for the dispersive transport [45] and the doping mechanism [6] as well. The basis for the model is the result that there are more T_3^0 centers in state B than in state A and no other center with unpaired spin has yet been detected in either state in undoped films at anywhere near the concentrations of neutral dangling bonds. The simplest explanation is a metastable trapping of photogenerated electrons *and* holes which yields excess T_3^0 centers. This requires the presence of stable T_3^+ and T_3^- centers in state A.

It should be noted that other unpaired spins can be present in sufficiently large concentrations, but these have not yet been detected by ESR. Furthermore, there could be more than one cause for photo-induced effects in a-Si:H alloys. In particular, the presence of certain impurities could catalyze additional effects not discussed in this paper. Nevertheless, the weight of present evidence is that the photo-induced effects in a-Si:H films are intrinsic and characteristic of bulk rather than interface properties.

6. Conclusions

There has been a plethora of experimental data on photo-induced effects in a-Si:H films, but a complete understanding is still sorely lacking.

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In fact, most of the proposed explanations for the origin of these effects possess major difficulties. In this paper, I have summarized many of the recent observations and have suggested a new model based on the specific structural and electronic characteristics of a-Si:H. In this model, no new defects are created by the light, but recombination of the photogenerated carriers induces excess neutral dangling bonds. These metastable centers are responsible for the increase in N_s, the change of E_F and most of the other experimental results.

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