Mechanisms for Peculiar Low-Temperature Phenomena in Hydrogenated Amorphous Silicon

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Concepts based on Si—H bond breakup (normal strength ~3.5 eV) or weakly bonded H have not accounted satisfactorily for many low-temperature phenomena: rapid decrease in the spin signal in the range 25–300 °C while the Si—H bond density is conserved or decreases; early H evolution stage at 200–450 °C and H diffusion, both with an activation energy of only 1.5 eV, etc. An elegant microscopic explanation of these and other phenomena is given in terms of a novel mechanism that is unique to the amorphous state: defect-mediated H diffusion during which the defects are annihilated.

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It is generally believed that the dominant paramagnetic center (*D* center) in amorphous Si (*a*-Si) is the dangling Si bond, that the density of *D* centers is reduced by H through the formation of Si—H bonds, and that H evolution occurs through the breakup of these bonds. Infrared spectra[1] and H-evolution data[2–6] in the range 450–700 °C support these concepts: H evolves with an activation energy of 3.4 eV,[6] close to the value in polyatomic molecules,[7] while the density of Si—H bonds decreases and the density of *D* centers increases. A number of other intriguing phenomena occur, however, at lower temperatures (25–450 °C) and have not been satisfactorily accounted for in terms of the above concepts.

In the range 200–450 °C, H diffuses with an activation energy that is only 1.5 eV.[8] In the same range, H evolution and a decrease in the density of Si—H bonds occur with an activation energy that is also 1.5 eV.[3–6] It has been suggested that these processes also occur via the breakup of Si—H bonds with either some kind of bond reconstruction[4,9] or H_2 formation[2,3] lowering the activation energy. Alternatively, weakly bonded forms of H have been invoked.[6] These suggestions have not been elaborated further and have obvious shortcomings.[10]

In the range 25–300 °C, high initial *D*-center density decreases rapidly while the Si—H bond density is conserved![4,5] The decrease in the *D*-center density persists to ~300 °C even though H evolution and a concomitant decrease in the Si—H bond density begin at ~200 °C. Yet H must be involved because a similar initial density of *D* centers in pure *a*-Si decreases ~50 times slower in the same temperature range.[11] No microscopic explanation for these intriguing phenomena is available.

Excess *D* centers created either by prolonged illumination (the Staebler-Wronski effect[12]) or by electron irradiation[13] also anneal in the range 100–250 °C with an activation energy of ~1.5 eV. The similarity of this activation energy with that of H diffusion and the possibility that H is involved in the annealing process have been noted,[12,13] but the mechanism that links the two effects has not been elucidated.

It is clear that no systematic explanation for the above phenomena exists. In fact, the most striking observations, such as the rapid decrease in *D* centers without any change in the density of Si—H bonds,[4,5] cannot be explained with the concepts that have been proposed thus far. The purpose of this paper is to propose a mechanism that explains the above phenomena in a systematic and elegant way. The key elements of this mechanism are *overcoordination,* a concept that until recently[14] was overlooked, and *diffusion mediated by intrinsic defects,* a process that occurs in crystals[15] but has not so far been explored in *a*-Si. It will be seen that low-temperature H diffusion, H evolution, and *D*-center annihilation have the same rate-limiting step, and hence a common activation energy. The annihilation of *D* centers that occurs while the density of Si—H bonds is conserved is due to a *unique effect that does not occur in crystals.* The observed two-stage H evolution follows in a natural way.

In crystalline Si (*c*-Si), intrinsic defects, mainly vacancies and self-interstitials, are known to mediate self-diffusion and impurity diffusion.[15] In *a*-Si, however, the role of intrinsic defects in mediating diffusion has not been explored. The dominant defect in *a*-Si has been universally believed to be threefold-coordinated Si or dangling bond, pointing into a microvoid or residing on an internal surface, with all the atoms on the "front side" being fourfold-coordinated and *too far to matter.* In such a picture, there is no obvious mechanism for a dangling bond to migrate with a small activation energy. Indeed, the migration of dangling bonds has not been used to explain the above phenomena.

It was recently[14] proposed that *overcoordination,* a concept that had been overlooked, occurs in *a*-Si and that threefold-coordinated Si atoms (dangling bonds) *and* fivefold-coordinated Si atoms (called floating bonds because of the distribution of the unpaired electron) are the primitive intrinsic defects.[16,17] It was shown that hyperfine EPR data favor the suggestion that the *D* centers are floating bonds. It will now be shown that overcoordination is also the key to understanding migration of intrinsic defects and that defect migration is, in turn, the key to understanding the phenomena mentioned earlier.

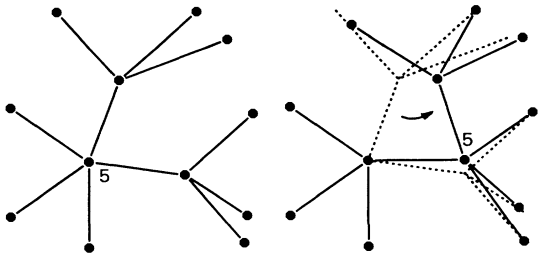

FIG. 1. Schematic illustration of floating-bond migration by bond switching.

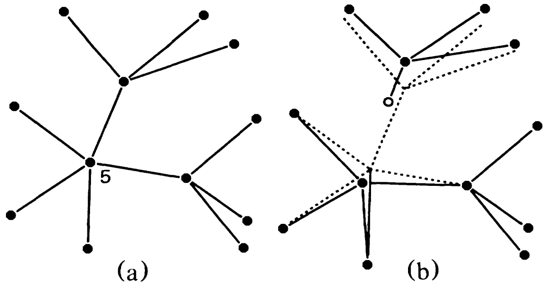

FIG. 2. A fivefold-coordinated Si atom (a) before and (b) after reacting with interstitial H. In the reverse reaction, the Si— H bond breaks up and a fivefold-coordinated atom is reformed.

Let us first consider floating bonds. Figure 1 shows schematically how floating bonds migrate easily by simple bond switching. *No particular fivefold-coordinated atom migrates through the network.* Instead, the extra bond is passed from one Si atom to another with only small atomic movements, so that the activation energy should be much smaller than bond-breaking energies. When a migrating floating bond gets passed to a Si atom that is already bonded to three Si atoms and one H atom, i.e., a standard Si— H bond, that particular Si atom has four Si nearest neighbors plus a H atom. Consequently, the H atom is no longer strongly bonded and is easily released in the interstitial regions. This reaction is analogous to the "kickout" mechanism in *c*-Si where the intrinsic defect is a self-interstitial:[15] A substitutional impurity such as P normally needs a large energy to break loose into the interstitial regions because it would leave behind a vacancy (four dangling bonds); a roving interstitial, however, can easily kick the impurity out and take its place. In *c*-Si, the reverse reaction also occurs, but not much else, so that the density of intrinsic defects is conserved. In *a*-Si:H, however, something unique occurs: When a roving H runs into a floating bond, it annihilates it by forming an Si— H bond. The reaction is shown schematically in Fig. 2: The H atom seeks the weakest of the five bonds and breaks it to form an Si— H bond and a fourfold-coordinated Si, for a net gain of energy. Thus, *migrating floating bonds mediate H diffusion and get annihilated, while the density of Si— H bonds is conserved.* This novel mechanism, which may be called "self-destructive mediation," is not possible in *c*-Si.

Let us now take another look at dangling bonds. As noted earlier, if the front-side neighbors are too far to matter, migration is all but impossible. If, however, one of the fourfold-coordinated front-side neighbors is not too far, the dangling bond might be able to pull it and make it a fourth neighbor, while one of the four original bonds of that atom break. It looks as if a dangling bond jumped over an atom, as in the case of vacancy migration in *c*-Si. Note that the key element of this process is overcoordination: The saddle point is fivefold-coordinated Si (the saddle point of vacancy migration in *c*-Si is sixfold-coordinated Si). Closer examination of this process, however, especially the need for interconversion[14] of a dangling bond into a floating bond, reveals that the total-energy fluctuations caused by dangling bonds are larger[18] than those caused by floating bonds. Luckily, for the purposes of this paper, a definitive choice between dangling and floating bonds need not be made. If we assume that dangling bonds can indeed migrate, we find that they also mediate H diffusion self-destructively: A migrating dangling bond reaches a Si— H bond and releases the H atom by forming a Si— Si bond; the H atom then migrates interstitially until it annihilates a dangling or floating bond by forming a Si— H bond.

In conclusion, migrating D centers, independent of whether they are floating bonds or *bulk* dangling bonds, undergo the reactions

$$D + \mathrm{Si_3H} \rightarrow \square + \mathrm{H}, \tag{1}$$

$$\mathrm{H} + D \rightarrow \square + \mathrm{Si_3H}, \tag{2}$$

where $\square$ denotes a fourfold-coordinated network and the subscripts denote coordination so that $\mathrm{Si_3H}$ is a standard Si— H bond. These two reactions, which rigorously define "self-destructive mediation," are the key to understanding the low-temperature phenomena mentioned earlier. In all cases, the rate-limiting step is the same (the migration of D centers or of unbonded interstitial H atoms, whichever costs more energy), which explains why so many seemingly disparate processes have roughly the same activation energy. More specifically, H diffusion occurs through the long-range migration of D centers as described by reactions (1) and (2). The activation energy is equal to the migration energy of D centers or of unbonded H atoms, whichever is larger. Thus, the observed value, ~1.5 eV,[8] cannot be assigned unambiguously at this time. The diffusion coefficient depends on the H content *and* the D-center density. Such a dependence was noted in Ref. 8, but additional data are needed as a test of the theory.

According to the reactions (1) and (2), as long as H evolution does not occur, H diffusion via migrating D

centers leads to a reduction of *D* centers, while the density of Si—H bonds is conserved. H evolution would, however, lead to a corresponding decrease in the Si—H bond density with only a slowdown in the ongoing decrease in the *D*-center density [because reaction (2) does not get a chance to occur]. That is precisely what is observed in the range 25–300 °C in samples with high initial density of *D* centers.[4,5] The *D*-center density decreases and the Si—H density is conserved in the range 25–200 °C where no H evolution occurs; the decrease in the *D*-center density persists up to ~300 °C even though H evolution and the concomitant decrease in the Si—H bond density begin at ~200 °C. The mechanism that underlies all this, namely reactions (1) and (2), further predicts that the activation energy for *D*-center reduction should be the same as that of H diffusion, ~1.5 eV. That is precisely what is observed in the case of the annealing of Staebler-Wronski excess *D* centers in the range 100–200 °C.[12] Annealing kinetics of *D* centers in experiments similar to those of Refs. 4, 5, and 13 would be a good test of the theory. Monitoring of the density of Si—H bonds by infrared absorption in experiments such as those of Refs. 12 and 13 would be another test.

In the range 200–500 °C, H evolution occurs with an activation energy of ~1.5 eV.[3-6] It happens because the H diffusion rate is now higher and also because, by ~200 °C, the density of *D* centers is depleted enough so that released H atoms are likely to reach the surface and evolve without running into a *D* center. The density of Si—H bonds is predicted to decrease in proportion to the H evolution rate, as indeed is observed.[3-6] The rate-limiting step for H evolution and the decrease in the Si—H bond density is again the same as for H diffusion; hence these processes have the same activation energy, as observed.[6]

At ~300 °C, breakup of Si—H bonds, requiring ~3.5 eV,[19] begins at an increasing rate.[6] This process leads to a monotonic increase in the *D*-center density. This effect constitutes the second stage of evolution, but, ironically, also slows down the rate of the first stage of H evolution. The slowdown occurs because all the H atoms that were already in interstitial sites on their way out are now more likely to be captured by the more abundant *D* centers. This competitive interplay suggests that the peak in the first-stage evolution rate should occur roughly when the *D*-center density goes through a minimum, as is indeed observed.[4,5] At even higher temperatures, of course, breakup of Si—H bonds occurs at a high enough rate to overwhelm the defect-mediated mechanism of the first stage, so that H evolution occurs with an activation energy of ~3.5 eV. Finally, the H content is depleted and the evolution rate slows down again. It is, therefore, possible to understand in detail the two-stage H evolution that is observed.[3-6]

In conclusion, we have seen that migrating *D* centers mediate H diffusion, which leads to annihilation of the *D* centers. This simple but remarkable phenomenon yields a systematic and elegant explanation of a large variety of data for most of which no explanation was available. A number of predictions were made calling for additional experimental tests. It should also be noted that the numbers available for activation energies,[4-6,12,13] though indicative of the correct order of magnitude, were extracted by kinetic modeling based on specific assumptions about the underlying reactions. The mechanisms described in this paper would be appropriate as the basis for systematic kinetic modeling of the data so that activation energies can be extracted in a more rigorous way. Finally, the migration of *D* centers is clearly responsible for similar phenomena that occur in fluorinated *a*-Si and in *a*-Ge. It is also likely to facilitate many other processes that occur in *a*-Si and *a*-Ge.

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[15] See, e.g., R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **54**, 360 (1985), and references therein.

[16] These ideas apply equally well to both continuous-random-network and microcrystalline (Ref. 9) models of the structure of *a*-Si. In the latter case, both dangling and floating bonds are in principle possible at grain boundaries.

[17] Floating bonds literally float through the network (Fig. 1), continually altering six-membered rings of atoms to five- or seven-membered rings and vice versa. Dangling bonds, on the other hand, cause major disturbances. To start with, a dangling bond must be part of an eight-membered or higher-order ring (the minimal microvoid), because the action of pulling a front-side neighbor closer divides the initial ring in two. One of these smaller rings then joins an adjacent ring to form a new high-order ring to accommodate the dangling bond in its new position. Actually, in the three-dimensional network, several such ring-order changes must occur simultaneously! Note also that, during migration, a dangling bond interconverts into a floating bond. The local total-energy fluctuation caused by a dangling bond is, therefore, at least as large as that of a floating bond. It is clearly larger, because the floating bond that results from interconversion of a dangling bond is quite contorted and stretched when compared with a normal floating bond (just like the sixfold-coordinated Si atom at the saddle point of the vacancy migration in *c*-Si has six bonds that are quite stretched by comparison with the bonds of the sixfold-coordinated Si atoms that occur when an extra Si atom occupies a hexagonal interstitial site).

[18] In a recent molecular-dynamics study of *a*-Si formed by rapid quenching, M. D. Kluge and J. R. Ray (unpublished) found ~25% of Si atoms to be fivefold-coordinated and no threefold-coordinated atoms.

[19] Breakup of Si—H bonds leading to recreation of a floating bond (the reverse reaction of Fig. 2) costs slightly less than simple Si—H breakup (Ref. 7), as indeed observed (Ref. 6).