Identification of Defects in Amorphous Silicon

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(Received 20 February 1990)

Defects in amorphous Si:H are identified by a new atomic model encompassing built-in defects and light-induced defects. The model consists of a metastable localized center having an atom with two possible sites, as in the Chadi and Chang model for *DX* centers in crystalline GaAs. Specific rehybridizations for two-site atoms produce changes in charge state and bonding that explain a wide range of effects, including *n*-type or *p*-type doping or compensation, the Staebler-Wronski effect and its variations with doping, quench-induced defects, and defect spin.

PACS numbers: 71.55.−i, 72.80.Ng, 78.50.Ge

Localized defects in alloys of hydrogenated amorphous silicon (*a*-Si:H) have been the objects of intensive study because of both their scientifically interesting properties and their impacts on applications of these materials. A major problem has been that defects can be introduced by poor preparation, quenching, doping, light exposure, or applied electric fields. Since these defects have major characteristics in common, there is reason to seek a common description for all defects. In good-quality *a*-Si:H these defects behave like localized, metastable centers with an energy difference between the two states of $\Delta E \approx 0.2$ eV. These centers have observable properties only when in their metastable state; one such property is an electron-spin resonance (ESR) with the same *g* value as that of a dangling bond on the surface of crystalline Si. Many defects have been found to be influenced by the presence of dopants, and the new model presented below is described primarily in that framework; effects other than dopants are discussed following this.

The present proposal for an atomic model for these defects in high-quality *a*-Si:H derives from the similarities of these stated properties to those of a theoretical model recently developed by Chadi and Chang for the metastable *DX* center in crystalline GaAs and AlGaAs alloys.[1,2] The key feature of that model is that a normal substitutional donor—whose electronic state is hydrogenic, or delocalized—can have a second configuration by rupturing one of its four normal bonds and moving to an adjacent, nearly interstitial site on the extended axis of the broken bond. (Actually, both atoms at the broken bond move from their ground-state positions, but one shift seems dominant and we focus here on that one.) In the second configuration the donor is threefold coordinated, and the center has a localized electronic state whose energy is "deep" in contrast to the "shallow" level of the substitutional site. Light can induce transitions from one state to the other, and heat can anneal out the metastable state. The energy difference between the two states is about 0.22 eV. This type of metastable center with a broken bond may occur at either Ga or As sites, and may describe the *EL*2 centers as antisite defects in GaAs[3,4] or self-compensating centers in *p*-type ZnSe.[5] These two-site centers are therefore not rare phenomena, and we expect an amorphous structure to have weaker steric constraints on the formation of special sites.

Because an amorphous structure is not amenable to the same kind of quantitative calculation, we examine the applicability of two-site centers to defects in *a*-Si:H by analogy. As is seen in the following, when such a model is supplemented by another important consideration—proper rehybridization—it provides simple, unified explanations for most properties of defects in *a*-Si:H. These explanations are considerably more comprehensive than in the preliminary account of this model.[6] Relations may also be seen to many earlier models, each of which can explain one or two observations. We first describe this two-site proposal for either column-III acceptors or column-V donors in *a*-Si:H. The hypothesis is that in the ground state of one of these centers the dopant is at a normal substitutional site with the tetrahedral configuration shown in Fig. 1(a), and thus has no observable *localized* electronic properties; i.e., it does not act as a defect. In this configuration the center is charged, positive for donors or negative for acceptors, and a conducting carrier has been released. In the metastable state, Fig. 1(b), one bond to a Si atom is broken, the dopant is threefold coordinated at a nearly intersti-

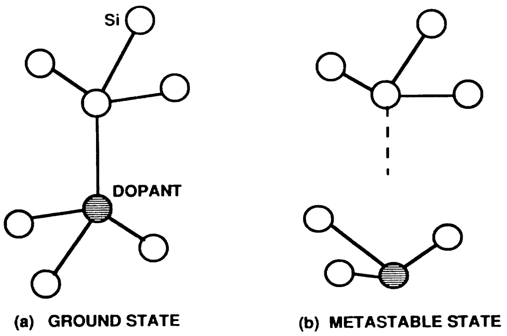

FIG. 1. The two configurations of a rehybridized two-site (RTS) center in *a*-Si:H. The dopant may be either a column-III acceptor or column-V donor. The dashed line is a dangling bond.

tial site, and the center is neutral.

These changes in bonding and charge state imply different hybridizations of the wave functions for the two configurations, differences that must be considered to complete this model. They are described most simply by an example in which the dopant is an acceptor atom (e.g., boron). In its ground state the center is negatively charged, and the B atom is at a tetrahedral site, with its fourth covalent sp^3 bond formed in the usual way by "borrowing" an electron from a bonding state of the host Si, leaving a conducting hole. In the metastable (neutral) state the B atom rehybridizes all of its valence wave functions (then primarily sp^2) to become threefold coordinated. Evidence from ESR indicates that the Si atom with the broken bond basically retains its sp^3 bonds to its remaining neighbors, and it is left with a "dangling bond" with only one electron. It is important that any model of these defects provides a center with a *neutral* dangling Si bond so as to be spin active; not all previous models do so. This dangling bond is localized and has a deep-level electronic state. Thus the formation of the metastable state from the ground state can be represented as

$$a^- + h^+ \rightarrow D^0, \tag{1}$$

where a^- represents the usual negatively charged acceptor, h^+ a neutralizing hole, and D^0 the neutral metastable defect.

For centers formed by donor atoms (e.g., phosphorus), this description is essentially the same; but rehybridization to form the metastable state *involves all five valence electrons* of the donor, so that an electron must be captured to form the metastable state. The relation between these two states is

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

It can be seen that the D^0 are configurationally the same for both donors and acceptors; only the central-cell potential identifies the particular atom involved.

One factor that eases formation of these metastable states is that both donors and acceptors favor threefold coordination. In fact, most dopant atoms in *a*-Si:H occupy *stable* threefold-coordinated sites that do not form defects. It may also be significant that the two most common dopants, boron and phosphorus, are small atoms and can most easily restructure this way. In all cases the asymmetry of the local structure about the broken bond is important and is a distinguishing feature of this model, as are these hybridizations and charge states. This asymmetry is a major difference between this model and the usual breaking of an ordinary Si-Si bond.

We refer to these centers as "rehybridized two-site" (RTS) centers; a RTS center in its ground state, RTS^g, replaces the "weak bond" of Si-Si bond-breaking models; and a RTS center in its metastable state, RTS*, is the "defect." The total number of RTS centers limits the number of defects that can exist; any change in density of RTS centers produces a proportional change in the density of defects. Because the energy difference for the two states is only $\Delta E \approx 0.2$ eV for the usual cases, the metastable state has an appreciable population in equilibrium at modest temperatures.

This model provides unified explanations for the following observations.

Generation of deep-level defects by doping, with either donors or acceptors.[7]—The clear evidence for dopant-induced dangling bonds in Ref. 7 is here a direct consequence of RTS centers that incorporate dopants. There is no need to invoke self-compensation as was done by Street,[8] and, in fact, the present proposal is a parallel to that of Chadi and Chang[5] in which two-site centers are a general alternative to the conventional model for self-compensation in crystals. In addition, this model leads to defects that are the metastable state of the centers, whereas Street's are in their ground state. Moreover, defects in the present model are limited in number because they arise at RTS centers, a significant difference from Si-Si-bond models.

Reduced density of defects in compensated materials.[7]—Reference 7 also showed that the dangling-bond density is very low in compensated *a*-Si:H, sometimes lower than in undoped material. When both donors and acceptors are present, carriers from each set become bound at the others and are therefore not available for conversion to RTS*. This need for free carriers to permit $\mathrm{RTS}^g \rightarrow \mathrm{RTS}^*$ has by itself several important consequences, some of which appear below.

Generation of defects by quenching (in uncompensated materials).[9]—The equilibrium population of RTS* at elevated temperature becomes quenched in upon cooling (as relaxation processes slow) and provides the observed built-in defects, as has been inferred from more general considerations without dependence on an explicit model.[10,11]

Generation of defects by light, the Staebler-Wronski (SW) effect.[12]—This model gives an explicit microscopic description to the well-known effects in which light, or carrier recombination, induces transitions to RTS*, and annealing restores RTS^g. Saturation in the density of SW defects reflects the limited number of RTS centers. Since saturation generally occurs at densities of only $\approx 10^{17}$ cm^{-3}, this is a key consideration and is treated in detail elsewhere.[13] This kind of defect "creation" is just a transformation within the localized center, and thus resembles a proposal by Adler,[14] although RTS centers have identifiable origins. A major attribute of the SW effect, the reduction of the dark conductivity in either *n*-type or *p*-type material caused by light exposure, is explained by the requirement of capture of a free charge in forming RTS*. This explanation of conductivity effects does not require that the electronic energy levels of defects in both *n*-type and *p*-type materials be at midgap. The decreased photoconductivity in the SW effect is, as usual, the consequence of an increased density of dangling bonds which act as recombination centers.

Doping dependence of the Staebler-Wronski effect.[15,16]—In Refs. 15 and 16, clear evidence was reported that higher doping results in a higher dangling-bond density produced by a given light exposure. This is explained by the doping-induced increase in the density of RTS centers, consistent with behavior shown in Refs. 10 and 11 to follow from general models, independent of microscopic details. At very high doping levels, however, occupation probabilities of the dangling-bond states may change, thereby altering these relationships, as reported in Ref. 15. Reference 16 also showed that compensated doping could result in fewer light-induced defects than in the best undoped *a*-Si:H. In the present picture for compensated material, carriers are diverted from the formation of defects by the availability of electronic states at energies below that of RTS*, thus reducing the number of defects, consistent with both Refs. 15 and 16. New experiments are planned to test these relationships.

Presence of a Si dangling bond[17] *in the metastable state and its spin.*[18]—The key here is the hybridizations in RTS*; threefold coordination of the dopant atom leaves a dangling bond on the Si atom.[17] The single electron in the dangling bond of a neutral RTS* makes it ESR active.[18] (In models such as Street's,[8] self-compensation requires that the defects be charged, so they would not be spin active.) The asymmetry of the RTS center results in only one dangling bond, not two as are expected in breaing a symmetric Si-Si bond, thus explaining the lack of spin-spin interactions between dangling bonds.

Although the foregoing accounts for all major dopant-related effects, defects occur without added dopants. Therefore, a complete identification of defects should eventually consider, for example, possible roles in defect formation of material-preparation conditions; hydrogen; voids; alloys with isoelectronic carbon or germanium; or the major impurities, oxygen and nitrogen. There are few quantitative data relating defects to these other factors, however, aside from attempts to correlate defects with H motion,[9] so we now consider qualitatively some of these effects in the context of this RTS model. Since the details of reconfiguration of RTS centers must depend on the structural properties of the host material as well as the moving atom, strains may influence the behavior of RTS centers. For example, the more stable state of the *DX* center actually switches under pressure or alloying.[2] Thus H concentration or alloying with C or Ge might effect the properties of these centers. Also, strain-induced effects on RTS reconfiguration will have parallel effects on diffusion, which involves a similar barrier.

The possibility that some of the host Si atoms may act as RTS centers needs to be considered: This is the familiar Si-Si bond breaking, with a new description for the metastable state. There are several difficulties, however. First, two dangling bonds would arise and interact, so they must be separated (perhaps by interchange with H). Second, the overwhelming number of Si atoms would mask all the dopant effects already discussed. Third, a low density of centers is implied by the saturation of light-induced defect density at low values ($\approx 10^{17}$ cm^{-3}) in good material. This density-limit problem is not removed by invoking only weak Si-Si bonds in a continuous distribution.[13] These difficulties would be reduced for a limited number of Si-Si bonds having local asymmetries. They could arise from a neighboring perturbation such as a void, a vacancy or interstitial, or an atom other than Si (e.g., a stable, threefold-coordinated dopant). This would be consistent with the findings that Si atoms can have a metastable state at an interstitial site either at the (111) crystalline Si surface[19] or near a Ga site in GaAs.[2] The most serious difficulty, however, is that there seems to be no rehybridization by which an initially neutral Si-Si bond can form a *neutral* dangling bond and reduce the conductivity as in the Staebler-Wronski effect.

For defects produced by nonoptimum material preparation, consideration of the general properties of RTS centers leads to the following testable proposal to explain this effect. First, for any model of these defects to have the same character as dopant-related RTS defects, a lower defect density should be accompanied by lower conductivity. The trend of improvements in *a*-Si:H quality has generally resulted in reductions in both conductivity and defect density, consistent with RTS centers, but we plan to test this prediction more quantitatively. Next, we note that nitrogen, as a column-V element, could form a RTS donor, and it is always present in sufficient quantities. As with other column-V atoms, N can take threefold coordination, but nonoptimum preparation may freeze in some fourfold-coordinated N atoms that could become RTS centers, accounting for the material being generally *n* type and for the sensitivity of the Fermi energy to preparation conditions. Some of these can anneal away irreversibly, as is observed, by shifting to *stable* threefold coordination. This proposal is not vitiated by the ambiguity of past searches for correlations of defects with N, because those tests did not include the variable of preparation conditions. We plan combined tests.

This RTS model suggests, therefore, the technologically hopeful conclusion that most defects are due to foreign atoms. Besides a unified explanation of many observations in *a*-Si:H, it also provides the conclusion that built-in and light-induced defects are parts of a single set with limited numbers. Important similarities are also established with defects in crystalline compounds and the new interpretation of self-compensation.

The authors wish to thank Walter A. Harrison for helpful discussions. This work was supported by the Electric Power Research Institute.

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