

## Hydrogen-mediated model for defect metastability in hydrogenated amorphous silicon

Sufi Zafar and E. A. Schiff

Department of Physics, Syracuse University, Syracuse, New York 13244-1130

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We propose a hydrogen-mediated model for defect metastability in hydrogenated amorphous silicon which associates the creation of paramagnetic defects with the transfer of hydrogen between the dilute and clustered phases of bonded hydrogen. Hydrogen in the clustered phase is predominantly paired on sites which we identify as weak Si-Si bonds when unhydrogenated. An elementary statistical-mechanics calculation based on this model accounts for the observed thermally activated paramagnetic defect density and also rationalizes the changes in spin density observed following electron irradiation and hydrogen evolution.

The paramagnetic defect density observed by electron-spin resonance (ESR) in undoped hydrogenated amorphous silicon (*a*-Si:H) exhibits large metastabilities. At room temperature the density can be increased by illumination, electron irradiation, or carrier injection, and above a characteristic temperature (about 200°C in undoped *a*-Si:H) the equilibrium spin density is thermally activated with an activation energy of order 0.3 eV.<sup>1</sup> Neither the microscopic identity of the defect nor the defect reactions which account for the changes in density are fully understood. The spin has usually been identified as a simple Si dangling bond, although some features of its electron-spin-resonance signature are more easily understood if the defect is a floating bond associated with an over-coordinated Si atom.<sup>2</sup> Several defect reactions have been proposed to account for the density changes, including changes in the sites to which hydrogen is bonded (the "hydrogen glass"),<sup>3-5</sup> creation of floating bond-dangling-bond pairs,<sup>6</sup> and creation of dangling-bond pairs.<sup>7</sup>

In this paper we present a hydrogen-mediated model for defect reactions based on the two known phases (dilute and clustered) of bonded hydrogen in *a*-Si:H. The model assumes that the underlying defect sites of the clustered phase are weak Si-Si bonds which preferentially bind hydrogen in pairs. As has been noted elsewhere,<sup>8</sup> hydrogen pairing on weak bonds is analogous to electron pairing on negative-correlation energy defects.<sup>9</sup> As we shall show, this model can semiquantitatively account for the interrelationships of three distinct experiments on the spin density in *a*-Si:H: electron irradiation, temperature dependence, and hydrogen evolution. The activation energy of the temperature-dependent spin density will be interpreted as the difference in the mean hydrogen binding energies of the two phases. We also discuss whether the ESR line shape in *a*-Si:H should be assigned to one or two distinct defect species; one feature of the present model which distinguishes it from some others is that only a single defect species needs to be observed by ESR.<sup>10-12</sup>

We first review the two phases of bonded hydrogen in *a*-Si:H. Infrared vibrational spectroscopy<sup>13</sup> indicates that for electronically optimized material nearly all the hydrogen is bonded to silicon atoms as *monohydrides* (only one hydrogen atom is bonded to a particular silicon atom). Nuclear-magnetic-resonance (NMR) spectroscopy indi-

cates that this bonded hydrogen is distributed in the material in two phases: a *dilute* phase of spatially isolated protons, and a phase of *clusters* of approximately six protons.<sup>14,15</sup>

In the present model, each of these clusters consists of three doubly hydrogenated sites on the surface of a microvoid. We shall term these sites *C* centers. These *C* centers are reconstructed as weak Si-Si bonds when stripped of hydrogen and we identify most weak bonds in *a*-Si:H with unhydrogenated *C* centers on the surface of microvoids. Similarly, we denote the hydrogen bonding site of the dilute phase as a *D* center. This term is usually used to indicate the principal paramagnetic defect in *a*-Si:H, and we extended the usage to apply to both the hydrogenated and unhydrogenated states. The proposed defect structures are shown in Fig. 1; for simplicity we assume that all structures are electrically neutral. Both for the *C* and *D* centers the hydrogenation state will be indicated by subscripted circles, filled to indicate hydrogenation and open if unhydrogenated. The *C* center has four hydrogenation states indicated as follows: a nonparamagnetic unhydrogenated or weak bond state ( $C_{\infty}$ ), two degenerate singly hydrogenated states ( $C_{\bullet\infty}$ ) which are paramagnetic, and a nonparamagnetic doubly hydrogenated state ( $C_{\bullet\bullet}$ ). The *D* center has an unhydrogenated, paramagnetic state ( $D_{\circ}$ ) and a singly hydrogenated, nonparamagnetic state ( $D_{\bullet}$ ).

Figure 1 also illustrates the proposed configuration coordinate diagrams of the *C* and *D* centers in various hydrogenation states. The important feature of the configuration coordinate diagram for the *C* center is that the first hydrogen attached to a *C* center (forming  $C_{\bullet\infty}$ ) is more weakly bound than the second (forming  $C_{\bullet\bullet}$ ). This assumption appears sensible, since the first hydrogenation energy of a weak bond ( $E_{\bullet\infty}^{\bullet}$ ) involves breaking of a bond whereas the second hydrogenation energy ( $E_{\bullet\bullet}^{\bullet}$ ) does not. Therefore, the following defect reaction should be exothermic:



If  $-\Delta \gg kT$ , this *negative hydrogen correlation energy* property implies that the density of paramagnetic  $C_{\bullet\infty}$  in thermal equilibrium is much smaller than the densities of

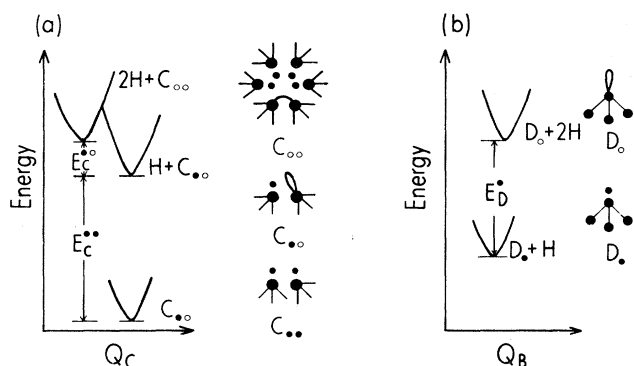


FIG. 1. (a) Right-hand side: The atomic configurations of the proposed  $C$  center in the unhydrogenated, singly hydrogenated, and doubly hydrogenated states  $C_{oo}$ ,  $C_{oo}$ , and  $C_{oo}$ , respectively; the  $C_{oo}$  state is a weak Si-Si bond. The  $C$  center is shown on the internal surface of a microvoid. Left-hand side: Configuration coordinate diagram for the  $C$  center for three hydrogenation states.  $H$  represents an unbonded interstitial hydrogen atom. Note that the first hydrogenation energy,  $E_C^{\bullet}$ , is smaller than the second ( $E_C^{\bullet\bullet}$ ) because of the breaking of the weak Si-Si bond required to form  $C_{oo}$ . (b) Right-hand side: The atomic configurations of the proposed  $D$  center (unhydrogenated  $D_o$ , hydrogenated  $D_{\bullet}$ );  $D_o$  is paramagnetic. Left-hand side: The configuration coordinate diagram of  $D$  center; the energy axes are the same as those for the  $C$  center.

either of the other two hydrogenation states of the  $C$  center.

Two experiments support the existence of Si defects with negative hydrogen correlation energy particularly clearly. In  $a$ -Si:H, hydrogen evolution during a 350°C anneal exceeds the associated increase in the spin density by a factor of 100 or more.<sup>16</sup> This observation can be explained if evolution primarily involves the conversion of  $C$  centers in the doubly hydrogenated state ( $C_{oo}$ ) to the weak bond or unhydrogenated state ( $C_{oo}$ ). Since neither of these states is detectable by ESR, the relatively small corresponding increase in the spin density will be addressed at the conclusion of this paper. This interpretation is reminiscent of less specific proposals of "bond reconstruction,"<sup>16,17</sup> an alternative mechanism involving recombination of migrating, floating, and dangling bonds following hydrogen evolution has been proposed by Pantelides.<sup>6</sup> Conversely, in very pure polycrystalline silicon, Jousse, Delage, and Iyer<sup>18</sup> has found that the hydrogen taken up by a specimen during subsequent plasma treatment is much greater than the corresponding decline of the spin density; we presume that hydrogen is taken up in pairs by an initial density of weak bonds.

In the remainder of this paper we shall describe the application of this two-phase model to the dependence of the measured spin density in  $a$ -Si:H upon temperature, electron irradiation, and hydrogen evolution. These applications are based upon textbook statistical mechanics calculations of the densities of the various hydrogenation states in the model in equilibrium with each other; the underlying total densities of  $C$  and  $D$  centers do not vary. The necessary symbols are defined in Fig. 2, which supplants

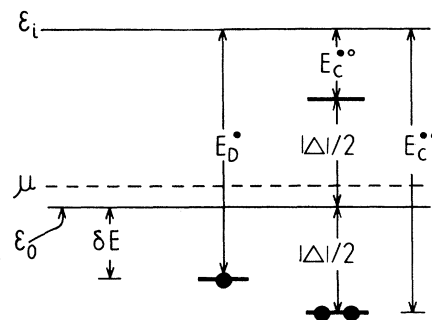


FIG. 2. Hydrogen energy-level diagram for  $C$  and  $D$  centers.  $E_C^{\bullet}$ ,  $E_C^{\bullet\bullet}$ , and  $E_D^{\bullet}$  are hydrogen binding energies defined in Fig. 1.  $\Delta \equiv (E_C^{\bullet} - E_C^{\bullet\bullet}) < 0$ .  $\epsilon_i$  is the energy level for unbonded hydrogen at an interstitial site.  $\mu$  is the chemical potential for the system of bonded hydrogen at thermal equilibrium.  $\epsilon_0$  is a reference level which lies midway between  $E_C^{\bullet}$  and  $E_C^{\bullet\bullet}$ ; the hydrogen binding energy for the  $D$  center lies  $\delta E$  below  $\epsilon_0$ .

Fig. 1 using the conventions of electronic energy-level diagrams. The  $C$  center has two hydrogen binding levels lying  $E_C^{\bullet}$  and  $E_C^{\bullet\bullet}$  below the interstitial level  $\epsilon_i$  (i.e., first and second hydrogenation energies). The  $D$  center has a single hydrogen binding level  $E_D^{\bullet}$  below  $\epsilon_i$ . The equilibrium densities of the various hydrogenation states can be obtained from the partition functions  $Z_D$  and  $Z_C$  describing the two centers with a common temperature  $T$ , and hydrogen chemical potential  $\mu$ :

$$Z_C = 1 + 2e^{-\beta(\epsilon_0 - \Delta/2 - \mu)} + e^{-2\beta(\epsilon_0 - \mu)}, \quad (2a)$$

$$Z_D = 1 + e^{-\beta(\epsilon_0 - \delta E - \mu)}. \quad (2b)$$

The total constant densities of  $C$  and  $D$  centers are denoted by  $N_C$  and  $N_D$ , respectively, and  $\beta = 1/kT$ . We shall use the notation  $N(C_{oo})$  for the density of singly hydrogenated  $C$  centers ( $C_{oo}$ ), and comparable forms for the densities of other hydrogenation states. For example,

$$N(C_{oo}) = (2N_C/Z_C)e^{-\beta(\epsilon_0 - \Delta/2 - \mu)}. \quad (3)$$

To apply this model to spin-density measurements in  $a$ -Si:H it is necessary to distinguish the contributions of the two paramagnetic hydrogenation states  $C_{oo}$  and  $D_o$ . Most ESR studies have concluded that the observed spin densities are attributable to a single type of defect.<sup>10-12</sup> It seems probable that the singly hydrogenated  $C$  center ( $C_{oo}$ ) would be distinguishable from the unhydrogenated  $D$  center ( $D_o$ ) by ESR, both because of the close proximity of the proton for the  $C_{oo}$  (with concomitant implications for the hyperfine structure) and because of differences in electronic structure of the  $D_o$  and  $C_{oo}$  (which should lead to distinct central line shapes).<sup>6</sup> We equate the measured spin density with the density of unhydrogenated  $D$  centers ( $D_o$ ), and neglect the contribution of  $C_{oo}$ . As will be discussed subsequently, the constraint that the density of  $C_{oo}$  is much smaller than the  $D_o$  density is satisfied if  $-\Delta \geq 1.2$  eV.

We applied this model to the temperature dependence of the spin density in  $a$ -Si:H. Experimentally, the density is activated above 200°C with an activation energy of or-

der 0.3 eV.<sup>1</sup> As the sample temperature is lowered below 200 °C, the spin density becomes essentially temperature independent, which has been interpreted as due to “freezing out” of hydrogen diffusion which maintained thermal equilibrium at higher temperatures. An activated temperature dependence emerges from the model when the spin density  $N(D_0)$  is much less than the weak bond density  $N(C_{00})$ . Assuming a constant total hydrogen density,  $N(C_{00})$  is then nearly temperature independent and the following useful form for the spin density  $N(D_0)$  can be obtained:

$$N(D_0)/N_D = [N(C_{00})/N_C]^{1/2} e^{-\delta E/kT}. \quad (4)$$

This equation describes the gradual transfer of bonded hydrogen from the dilute phase to unhydrogenated weak bonds of the clustered phase as the temperature is raised. The measured activation energy for the thermal equilibrium spin density estimates the model parameter  $\delta E$  (cf. Fig. 2); the physical interpretation is that the hydrogen binding energy of the  $D$  center exceeds by  $\delta E$  the mean of the two binding energies of the  $C$  center.

The remaining applications of this model are based upon Fig. 3, which presents the predicted densities at 200 °C of several hydrogenation states as a function of chemical potential using our best estimates for the model parameters  $N_D$ ,  $N_C$ ,  $\delta E$ , and  $\Delta$ . We used  $\delta E = 0.36$  eV, which is in the range of thermal activation energies obtained from temperature-dependent spin-density measurements.<sup>1</sup>  $N_D$  and  $N_C$  were equated to the measured densities of dilute and clustered phase sites as determined by NMR.<sup>14,15</sup> Reported values are comparable in all device-grade  $a$ -Si:H; we used  $N_D = 10^{21}$  cm<sup>-3</sup> and  $N_C = 5 \times 10^{20}$  cm<sup>-3</sup>. The precise negative value for  $\Delta$  is not critical; for  $|\Delta| > 1.2$  eV the (paramagnetic) density of  $C_{00}$  remains below  $2 \times 10^{14}$  cm<sup>-3</sup> for all values of the chemical potential. We have chosen 200 °C for this figure because the “freeze-in” phenomenon mentioned earlier suggests that calculations at this temperature are best for comparison to density measurements at room temperature.

Figure 3 rationalizes two effects found in electron irradiation and hydrogen evolution experiments. Schneider, Schroder, and Finger<sup>19</sup> found that the spin density in a particular specimen of  $a$ -Si:H could be increased from  $5 \times 10^{15}$  cm<sup>-3</sup> to a saturated value of  $10^{18}$  cm<sup>-3</sup> by irradiation with 20 keV electrons. If this experiment is interpreted as driving hydrogen from  $D_{00}$  onto  $C_{00}$  in pairs, then saturation may be identified with occupation of all previously unoccupied  $C_{00}$  weak-bond sites. This interpretation leads to an estimate of the weak bond density of  $5 \times 10^{17}$  cm<sup>-3</sup> in a sample with spin density of  $5 \times 10^{15}$  cm<sup>-3</sup>. Inspection of Fig. 3 indicates that these two values are consistent for  $\mu - \epsilon_0 = 0.15$  eV.

Similarly, hydrogen evolution experiments in device-grade  $a$ -Si:H indicate that low-temperature annealing increases the spin density from about  $5 \times 10^{15}$  cm<sup>-3</sup> to  $10^{17}$  cm<sup>-3</sup> while approximately  $10^{20}$  cm<sup>-3</sup> hydrogen atoms are evolved.<sup>16</sup> Using Fig. 3, this phenomenon can be in-

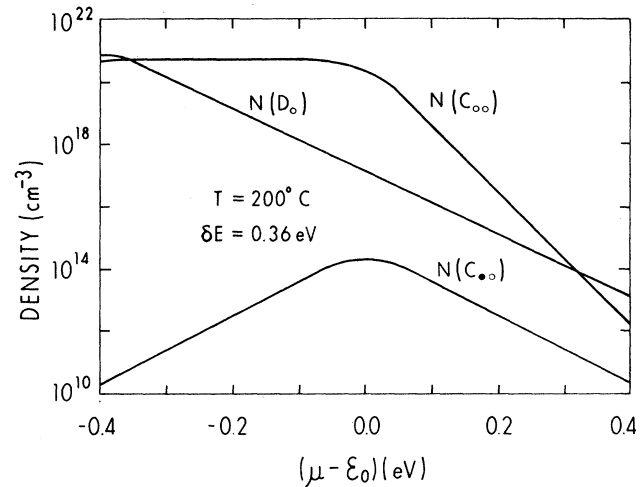


FIG. 3. Calculation of the densities of paramagnetic  $D$  centers  $N(D_0)$ , weak bonds  $N(C_{00})$ , and singly hydrogenated  $C$  centers  $N(C_{00})$  as a function of the hydrogen chemical potential  $\mu$  at 200 °C.  $\delta E = 0.36$  eV,  $\Delta = -1.2$  eV,  $N_C = 5 \times 10^{20}$  cm<sup>-3</sup>,  $N_D = 10^{21}$  cm<sup>-3</sup>.

terpreted in the following way. Low-temperature hydrogen evolution corresponds to motion of the chemical potential from the right-hand side toward the center of Fig. 3. In this regime inspection of Fig. 3 indicates that the hydrogen evolves almost entirely from doubly hydrogenated weak bonds ( $C_{00}$ ); the hydrogen evolved is twice the increase in the weak bond density  $N(C_{00})$ . The initial spin density of  $5 \times 10^{15}$  cm<sup>-3</sup> in the hydrogen evolution experiment corresponds to  $\mu - \epsilon_0 = 0.15$  eV in Fig. 3. As hydrogen evolves, the chemical potential decreases and near  $\mu - \epsilon_0 = 0.0$  eV the spin density and hydrogen evolution reach  $10^{17}$  cm<sup>-3</sup> and  $10^{20}$  cm<sup>-3</sup>, respectively, in agreement with the experimental magnitudes noted above.

The particular hydrogen-mediated model we have presented thus appears to offer reasonable explanations for a variety of experimental results. Perhaps its most attractive feature is that it is a hydrogen-mediated model which invokes both phases of bonded hydrogen observed by NMR. An obvious refinement of the model would be to include distributions of hydrogen binding energies for the two phases, although at present this refinement appears unnecessary. An important challenge for this model will be to ascertain whether it can form the basis for understanding the kinetics of nonthermal defect density changes produced near room temperature by illumination and other excitations.

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