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Role of Bonded Interstitial Hydrogen in Hydrogenated Amorphous Silicon: A New Perspective†

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We propose that the intersititial hydrogen bonded to a fourfold coordinated silicon atom exists in hydrogenated amorphous silicon (a-Si:H). We point out that the dopant atoms in a-Si:H can be passivated by the interstitial hydrogen. The motion of the bonded interstitial hydrogen is the underlying mechanism in most metastable-defect processes. We show that microscopic models consisting of bonded interstitial hydrogen are able to explain a number of unresolved issues: the variation of thermally induced band-tail carriers is dominated by the change of dopants rather than by dangling bonds which are independent of temperature; the shortcomings of the weak Si-Si bond-dangling bond conversion model for photodegradation process; the peculiar phenomena in hydrogen evolution, such as the density of dangling bonds decreasing without any change in the density of Si-H bonds.

Incorporation of hydrogen into amorphous silicon (a-Si) reduces the density of dangling bonds by several orders of magnitude, and it also leads to the substitutional doping of hydrogenated amorphous silicon (a-Si:H) [1]. In addition, the presence of hydrogen in a-Si:H causes many peculiar phenomena not commonly observed in other materials. For example, in doped samples hydrogen diffusion leads to the stretched exponential relaxation of bandtail carriers [2]. It is believed that the motion of hydrogen is the underlying mechanism of most metastable-defect processes [3]. Obviously, the bonding configuration of hydrogen is very important for the understanding of the optical, electronical, thermal equilibration, and device properties in a-Si:H.

Even though it is well established that hydrogen does play a very important role in a number of phenomena in a-Si:H, the exact microscopic mechanisms are still unclear, and several issues remain to be resolved. For example, the thermally induced variation in band-tail carriers in doped samples are dominated by changes in the density of dopant atoms

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rather than by dangling bonds which are almost independent of temperature [4]. Shortcomings exist in the weak Si-Si bond-dangling bond conversion to explain photodegradation [5]. A rapid decrease in the density of dangling bonds without any change in the density of Si-H bonds is found in the studies of infrared spectra and hydrogen evolution data [6].

In this paper, we introduce a new viewpoint, motivated by extensive recent results on hydrogen in crystalline semiconductors [7], and propose that both the hydrogen bonded to a threefold coordinated Si atom denoted as Si_3-H, which is a normal configuration of Si-H bond, and the interstitial hydrogen bonded to a fourfold coordinated Si atom denoted as Si_4-H exist in a-Si:H. We suggest that the dopant atoms in a-Si:H can be passivated by the interstitial hydrogen. We propose that the motion of the bonded interstitial hydrogen is the underlying mechanism for metastable-defect processes in a-Si:H, and it can be considered to form a seperate substructure that has properties similar to a glass [8]. We show that the microscopic model consisting of the motion of the bonded interstitial hydrogen can explain the above unresolved phenomena in a systematic way.

Recently, hydrogen in crystalline silicon (c-Si) has been studied very extensively [7,9,10]. From ion-channeling measurements on deuterium (D)-implanted c-Si, Picraux et al. [9] showed that the D is located predominantly in a single interstitial site 1.6 $\AA$ along a $< 111 >$ direction from a Si atom in the antibonding direction. Indeed, the tight-binding calculations by Johnson et al. [10] indicate that the bonding of H to Si in an antibonding site along the $< 111 >$ axis is energitically favorable and the bond length is 1.61 $\AA$ which is in excellent agreement with the experiment. The calculated Si-H stretch vibrational frequency of the above D center is 96.7% of the normal Si-H frequency which can explain several vibrational modes of disputed origin observed in H-implanted c-Si [10]. Thus, it is reasonable to believe that Si_4-H complex formation does exist in c-Si. The high quality a-Si:H contains a relatively high hydrogen concentration (order of 10 %) which are incorporated relative to the smaller number of dangling bonds as measured by electron-spin resonance (ESR) [11]. Since the local enviroment of a-Si:H has the short range order which is very similar to that of c-Si, we thus propose that the interstital hydrogen bonded to a fourfold coordinated Si atom exists in a-Si:H. We assume that Si_4H complex in a-Si:H has the same properties as in c-Si. The electronic structure for Si_4H complex is an acceptor [10], the complex becoming negatively charged and creating a hole some distance away. Thus, the fact no ESR signal of Si_4H has been observed is a result of this spin-paired configuration. From tight-binding calculation [10], the binding energy of Si_4H is about 1.5 eV, which is much smaller than that of Si_3H, 3.4 eV. If the basic diffusion step of the hydrogen atom is directly hopping from one interstitial bonded site to another, the hopping energy required to release hydrogen atom from a Si_4H bond is therefore equal to the activation energy of diffusion. In fact, the binding energy of Si_4H, 1.5 eV, is consistent with the activation of

hydrogen diffusion in a-Si:H [12,13]. The energy needed to break a Si_4H bond is doping dependent as indicated by Street et al. [13]. Since hydrogen diffusion is believed to be responsible for many metastable-state creations, we thus propose that the motion of the hydrogen in Si_4H complex is the underlying mechanism for metastable-defect processes in *a*-Si:H, and it can be considered to form a separate substructure that has properties similar to a glass [8]. We also suggest that Si_4H complexes are responsible for the hydrogen evolution at low temperatures since their binding energy is smaller than that of Si_3H. From the data of hydrogen evolution [6] the estimated concentration of Si_4H is in the order of $10^{19}\,cm^{-3}$ in high quality a-Si:H film which is much larger than that of dangling bonds, $10^{16}\,cm^{-3}$, and is much smaller than that of Si_3H complexes, $10^{21}\ cm^{-3}$. Note that in the Si_4H complex, the Si atom is overcoordinated. It has been pointed out that overcoordination cannot be ruled out on the basis of having only s and p electrons, since high-coordination Si phases exist in many materials [14], such as floating bond porposed by Pantelides [14].

It is well known that hydrogen can passivate shallow impurities in a variety of crystalline semiconductors which has created intensive interest in this area [7]. The microscopic structures of hydrogen bonding with ***B*** and ***P*** dopants in c-Si have been determined. In B-doped c-Si, an interstitial H atom is near the bond-center site between the substitutional ***B*** and the neighboring Si atoms [15]. In P-doped c-Si, an interstitial H atom is near an antibonding site of a-Si atom adjacent to the substitutional P^{10}. Here, again the key element is the interstitial hydrogen. In analogy to c-Si, we propose that the dopant atoms in a-Si:H can also be passivated by interstitial hydrogen.

Let us now examine the problems in metastable thermal equilibrium. It has recently been demonstrated by the Xerox group that the defect structure of doped a-Si:H is in metastable thermal equilibrium, having temperature-dependent densities of band-tail carriers and donor or acceptor states, and the dangling bonds in the films do not dependent on temperature [2,4]. The time to reach equilibrium is thermally activated, becoming longer at lower temperature. As the samples are cooled following a high-temperature anneal, two regimes of behavior separated by a temperature T_e are observed. T_e is the temperature at which the defect structure comes into equilibrium in a few minutes. Above T_e the electronic properties are independent of the prior thermal history of the sample. Below T_e **a** nonequilibrium slowly relaxing electronic and atomic structure is frozen in. The slow relaxation follows a stretched exponential time decay and has been attributed to the dispersive diffusion of bonded hydrogen (Si_3-H). The Xerox group shows that the defect-compensation model of doping provides an accurate phenomeno-logical description of the results. They propose that the motion of bonded hydrogen is important, and that it can be considered to form a separate substructure that has properties similar to a glass. In the hydrogen glass model, the bonded hydrogen (Si_3-H) moves locally from site to site. and the breaking of

the weak Si-Si bond by the H is the dominant mechanism in thermal equilibrium. Even though the model can account for the most behaviors of the thermal equilibrium process, there still remain some unresolved issues.

The defect-compensation model is based on the assumption that both the density of dangling bonds and active dopants depend on the Fermi-level position. Street [16] proposed that in doped a-Si:H, phosphorus (or boron) could be incorporated into the growing film in either three-fold or four-fold coordination, and in order to obey a modified 8-N rule a fourfold-coordinated dopant can exist only when at the same time a dangling-bond defect is created. According to this model the density of band-tail carriers n_{BT} is fixed by the density of dopants, N_D, and of dangling bonds N_{DB}, to an approximation by

$$n_{BT} = N_D - N_{DB}. \quad (1)$$

The results of photothermal deflection spectroscopy, capacitance-voltage characteristics, and bias - annealing measurements on samples annealed and quenched at different temperatures show that the equilibration of n_{BT} is dominated by changes in the density of dopants rather than by dangling bonds which are almost independent of temperature [4]. Based on the above model, the expected observable range of N_{DB} is about 100. Evidently, the model has difficulty in accounting for the temperature independence of the dangling-bond density.

Structually, an electronically-active dopant atom in a-Si:H requires an approximately tetrahedral bonding enviroment; therefore, doping induced dangling-bond defects must be spatially separated from the dopant atoms. As the Fermi level moves into either one of the band tails due to dopant atoms, weak bonds will either loose their bonding electrons, or their antibonding states will become occupied. This, of course, can cause the weak bond to be eliminated in favour of additional dangling bonds [17]. Here the dangling bond formation is only a secondary effect of the doping process, and not a regulatory mechanism as the above model.

From the study of hydrogen diffusion, it is found that the diffusion coefficient D_H is activated with an energy of 1.2-1.3 eV in doped a-Si:H [13]. This implies that the energy to break a Si-H bond must have about the same energy. From infrared spectra and H-evolution data in the range of 450-700 °C, H envolves with an activation energy of 3.4 eV, while the density of Si_3-H bonds decreases and the density of dangling bonds increases [18]. It is reasonable to believe that to break a Si_3-H bond requires about 3.4 eV. Thus, it is not easy to see why hyrogen diffuses at relatively low temperatures and low activation energy.

In the following we provide a microscopic mechanism of equilibration which includes the Si_4H complex and propose that the motion of this bonded interstitial hydrogen is the underlying mechanism of equilibrium. We are able to overcome the above difficulties.

If we assume that the dopant atoms in a-Si:H can be passivated by hydrogen, the thermally induced variations in n_{BT} is controlled by the passivation and reactivation of

dopant atoms by the interstitial hydrogen without the change of dangling bonds, according to the reactions

$$Si_3P_4^+ + e^- + Si_4H \rightleftharpoons HSi_3P_4 + Si_4, \quad (2)$$

$$Si_3B_4^- + e^+ + Si_4H \rightleftharpoons Si_3HB_4 + Si_4, \quad (3)$$

where P_4^+ and B_4^- represents the active dopants. This can account for the experimental fact that the equilibration of n_{BT} is dominated by changes in the density of active dopants rather than by dangling bonds which are independent of temperature. In addition, this allows for the possiblity that the creation of dangling bonds by doping is only a secondary reaction of a-Si:H to the presence of the doping atoms, rather than a necessary condition for the formation of active dopants.

In the model here, the motion of bonded interstitial hydrogen has binding energy about 1.5 eV which is consistent with the activation energy of the hydrogen diffusion in a-Si:H. Note that the activation energy of the time constant for the stretched exponential relaxation of n_{BT} is about 1 eV which is different from the above value. This difficulty has been resolved by Jackson [17] using the concept of dispersive transport of hydrogen.

We turn now to the photodegradation in a-Si:H which is also known as the Staebler-Wronski effect [20]. Present attempts to model this effect microscopically have centered on the weak Si-Si bond - dangling bond conversion and the bond breaking is stablized by hydrogen [17,21-23]. One of the models is that a weak Si-Si bond breaks when it traps the excess carriers, and a bonded hydrogen in the configuration of Si_3-H moves toward the site of the weak bond and terminates one of the dangling bonds [17]. The second mechanism is that the release of a bonded hydrogen is enhanced by the excess carriers, and it moves from site to site and inserts into a weak Si-Si bonds, thus two dangling bonds are created [23]. The shortcoming of the first model is that the band-tail carriers not only break the weak Si-Si bonds, but must also open up a H diffusion path involving these bonds. In addition, to release hydrogen from Si_3-H bond, requiring about 3 eV, is very unlikely below room temperature. For the second mechanism, it is not quite easy to see why the carriers in the band tails, i.e. in the bonding and antibonding states of weak Si-Si bonds don't break these bonds but instead the stronger Si_3-H bonds. However, if we assume that it is the motion of hydrogen released from Si_4-H site that breaks the weak Si-Si bond, and the trapping of the excess carriers in the weak Si-Si bond is to reduce the bonding strength which will be broken by the atomic hydrogen, the above difficulties of the two models can be resolved. The reaction is as following

$$Si_4H + e^+ + Si_3Si_3 \rightleftharpoons Si_4 + Si_3^+ + Si_3H. \quad (4)$$

Here the bonding energy of Si_4-H is low so that the hydrogen can move at relative low temperature. In addition, hydrogen diffusion and formation of dangling bonds are essentially the same process. The problem of the separation of the two dangling bonds needed for thier metastability in the previous models does not exist in our model.

As pointed out by Pantelides [14], number of intriguing phenomena of infrared spectra and H-evolution data occur at temperatures in the range 25-450 °C. In the range 25-200 °C, high initial dangling bonds decrease rapidly while the infrared absorption of the Si-H stretch vibrational mode (2000 cm^{-1}), α_{2000}, is conserved [G]. The decrease in the density of dangling bonds persists to 300 °C even though H evolution and a concomitant decrease in the α_{2000} begin at $\sim$ 200 °C[6]. In the range 200-450 °C, H evolution and a decrease in the α_{2000} occur with an activation energy that is also 1.5 eV[18]. There is no systematic explanation for the above phenomena except that a model is of interest which has recently been proposed by Pantelides [14]. The key elements of his mechanism are so-called floating bond located on fivefold coordinated Si atoms. In contrast to the usual picture that the spin centers are the dangling bonds, i.e. threefold coordinated Si atoms, he points out that these defects do not have a spin because of a negative correlation energy and that the signal of electron spin resonance with g=2.0055 is due to floating bonds. Even though this model has attractive features, it is problematic. Evaporated a-Si has a spin density of up to 10^{20} cm^{-3}[24] and at such a high density of pairs the two defects, dangling bonds and floating bonds, should easily recombine since the floating bonds are assumed to be highly mobile. Consequently the spin density should decrease an order of magnitude by annealing at fairly low temperature which is not observed. Thus the model requires that in pure a-Si the density of dangling bonds is much smaller than that of the floating bonds. The assumption of up to $10^{20}\,cm^{-3}$ overcoordinated network atoms does not fit into the general picture of disordered covalently bonded semiconductors [5]. Here we propose a mechanism that explains the above phenomena in a systematic and elegant way. Again, the key elements of the mechanism is interstitial hydrogen bonded to a fourfold coordinated Si atom.

In the following we will adapt the Pantelides' esplanation, but the floating bond in Ref. 14 is replaced by Si_4H bond. Even though the statement is a repitition of that by Pantelides [14], we still present it here to show how the Si_4H bond can explain the peculiar phenomena. We will not distinguish the infrared vibrational modes between Si_3H and Si_4H even their binding energy are different. The calculated Si-H stretch vibrational frequency of Si_4H is about 96.7 % of that of Si_3H in c-Si [10]. This small difference may be washed out by the disorder characteristic in a-Si:H, and the observable decrease of the infrared absorption of Si-H stretching mode (2000 cm^{-1}) $\sim$ 200 °C, which is too low to release H from a Si_3H configuration, can be accounted for the release of hydrogen from Si_4H. According to reaction (5) the motion of the bonded interstitial hydrogen leads to terminate a dangling bond and

to reduce the density of dangling bonds, while the α_{2000} is conserved.

$$Si_4H + Si_3 \rightarrow Si_4 + Si_3H. \quad (5)$$

H evolution would lead to a corresponding decrease in the α_{2000} with only a slowdown in the ongoing decrease in the density of dangling bonds. That is precisely what is observed in the range 25 – 300° C in samples with high initial density of dangling bonds [6]. The dangling bonds decrease and the α_{2000} is conserved in the range 25 – 200 °C where no H evolution occurs; the decrease in dangling bonds persist up to 300 °C even though H evolution and the concomitant decrease in α_{2000} begin at ~ 200 " C. In the range 200-450 °C, H evolution occurs with an activation energy of ~ 1.5 eV[18]. It happens because the H diffusion rate is now higher and also because, by ~ 200 °C, the dangling bonds are depleted enough so that released H atoms are likely to reach the surface and envolve without running into a dangling bond. The α_{2000} is predicted to decrease in proportion to the H evolution rate, as indeed is observed [6]. The rate limiting step for H evolution and the decrease in the α_{2000} is the same as for H diffusion; hence these processes have the same activation energy, as observed [18]. At ~ 300 °C, break up of Si_3-H bonds begins at an increasing rate. This process leads to a monotonic increase in dangling bonds. This effect constitutes the second stage of evolution, but slows down the rate of the first stage of H evolution. The slowdown occurs because the H atoms now more likely to be captured by the more abundant dangling bonds. This competitive interplay suggests that the peak in the first-stage evolution rate should occur roughly when the dangling bonds goes through a minimum, as is indeed observed [6].

In summary, we showed that motion of interstitial hydrogen bonded to a fourfold coordinated Si atom forms the cornerstone of microscopic models for the systematic description of many unresolved issues in a-Si:H, thermal equilibrium process, photodegradation, and hydrogen evolution. We also propose that the dopant atoms in a-Si:H can be passivated by the interstitial hydrogen which is very important for the understanding of doping phenomena. Thus, we believe that the motion of bonded interstitial hydrogen atoms is the underlying mechanism for most metastable-defect processes observed. More theoretical and experimental studies along the line shown here, may improve our understanding about a-Si:H and other hydrogenated materials, such as a-Ge:H, a-SiGe:H, ··· etc.

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