

## Reactivation Mechanisms for Shallow Impurities in Hydrogenated Crystalline Silicon

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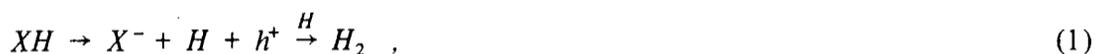
We point out that a correct mechanism for the reactivation of shallow impurities in hydrogenated crystalline silicon has to interpret the facts that the activation energy of the reactivation is about  $1.4\text{eV}$  which does not depend on the type of dopants and dopant species, the reactivation rate can be enhanced by minority carrier injection or light illumination. The current mechanism is intuitive and is unjustified by the experimental facts. A microscopic model for the reactivation involving hydrogen-related complexes which do not contain any other impurities is proposed. Reactivation of shallow impurities occurs when this complex dissociates creating interstitial hydrogen atoms which diffuse rapidly to hydrogen-impurity complexes and break hydrogen-passivating bonds, and thus a hydrogen molecule is formed. A possible candidate of this hydrogen-related complex involving two-hydrogen-atom complexes is also suggested.

Introduction of atomic hydrogen into semiconductors can significantly change the electrical and optical properties of the materials.<sup>1</sup> For instance, it leads to the development of technical applications of amorphous silicon.<sup>2</sup> The principle interest in crystalline semiconductors occurs because of its ability to passivate the electrical activity of dangling or defective bonds. It is also found that hydrogen can passivate both shallow acceptor and donor impurities in many technologically important semiconductors.<sup>3</sup> Since hydrogen is present during many processing steps for fabricating modern semiconductor devices, its potential effects should be thoroughly understood. Furthermore, we have shown that hydrogen can be used as a sensitive probe of defect reactions providing an exciting opportunity to clarify defect microstructures.<sup>3</sup> Thus, in recent years, the incorporation of atomic hydrogen into semiconductors has attracted wide interest. An extensive review on this topic has been written by Pearton et al.<sup>4</sup>

From a fundamental point of view, it is attractive to study the interaction between hydrogen, the most elementary atom, and silicon, the prototypical semi-conductor. Thus hydrogen passivation in crystalline silicon has become a model case in this field. In the last few years, the theoretical and experimental investigations of hydrogen passivation effects

and the structures of hydrogen-impurity complexes in silicon have been studied extensively.<sup>4-20</sup> Hydrogen was found to passivate shallow impurities such as boron, aluminum, gallium, phosphorus, arsenic, antimony, etc., leading to an increase in resistivity. The structures of the hydrogen-shallow-impurity complexes have been widely debated and have become the best understood among hydrogen-containing complexes in semiconductors because of a large body of theoretical and experimental studies. For hydrogen-acceptor complexes in silicon, most studies agree that hydrogen occupies a bond-centered site between the acceptor atom and one of its silicon neighbors, and hydrogen atom can move relatively freely around the substitutional impurity. This model was originally proposed by Pankove et al.<sup>4</sup> and was later modified slightly.<sup>16,17</sup> Even there are some evidence<sup>9,22</sup> showing that a small percentage of hydrogens locates at antibonding or tetrahedral interstitial site, but this observation is attributed to the damage induced by hydrogen atoms. For hydrogen-donor complexes, the hydrogen atom is attached to one of the donor's nearest neighbors and occupies the antibonding position along the (111) axis containing the donor atom, with the silicon-hydrogen pair relaxing away from donor, leaving the donor atom threefold coordinated.<sup>5,19,20</sup>

After establishing the atomic structures of hydrogen-impurity complexes, the next interesting question to be investigated is the reaction of shallow impurities. An understanding of the reactivation mechanism can provide not only the information of the stability of hydrogen-impurity complexes but also the interactions between hydrogen and host atoms and impurities. To our knowledge, the current model for the reactivation of the impurities in silicon is the direct dissociation of hydrogen from a hydrogen-impurity complex according to the following reactions,<sup>6,17,23</sup>



and



where X denotes a shallow impurity, and  $h^+$ ,  $e^-$  are a free hole and electron, respectively. However, this intuitive model is unjustified. It has difficulty to explain several experimental results as shown below. In the remainder of this paper we will present the data that have to be explained, and we will point out the deficiencies of the intuitive model. A possible mechanism for the reactivation of shallow impurities in silicon is then proposed.

Let us first summarize the key experimental results that need to be accounted for.

(1) At liquid helium temperature, the stretching vibrational frequencies of acceptor-hydrogen complexes for the group III acceptors, B, Al and Ga are  $1907 \text{ cm}^{-1}$ ,  $2201 \text{ cm}^{-1}$ , and  $2171 \text{ cm}^{-1}$ , respectively,<sup>7</sup> while that of donor-hydrogen complexes for the group V donor, P, As, and Sb are  $1555.2 \text{ cm}^{-1}$ , and  $1561.0 \text{ cm}^{-1}$ , and  $1561.7 \text{ cm}^{-1}$ , respectively.<sup>13</sup> These results indicate that the binding strengths of acceptor-hydrogen and donor-hydrogen

complexes are quite different, which can be easily understood from their atomic configurations as discussed above. Indeed, Chang and Chadi<sup>16</sup> calculated the binding energies of B-H complex and P-H complex to be 2.5eV and 2.0eV, respectively. They also used this result to explain the fact that hydrogen passivation is more effective in p-type than in n-type silicon.

(2) The activation energies for reactivation of acceptor-hydrogen complexes for the group III acceptors, B, Al, Ga, and In are 1.28eV, 1.44eV, 1.40eV, and 1.42eV respectively,<sup>23</sup> for the donor-hydrogen complexes of P, As, and Sb, they are 1.32eV, 1.43eV, and 1.43eV, respectively.<sup>13</sup> In both cases, the same value of attempt frequencies ( $10^{13}s^{-1}$ ) were used. From this result, we can see that even the activation energies show slight variation, but all of them have the value of about 1.4eV. Thus, it indicates that the activation energy for reactivation of shallow impurities does not depend on the type of dopants and the dopant species. More surprisingly, it has been found that the activation energies for reactivation of the neutralized chalcogen-impurity-hydrogen complexes are as follows: For isolated substitutional sulfur, selenium, and tellurium, the energies are  $1.61 \pm 0.2eV$ ,  $1.39 \pm 0.17eV$ ,  $1.39 \pm 0.18eV$ , respectively, and for the pure pairs of sulfur and selenium, they are  $1.56 \pm 0.2eV$  and  $1.41 \pm 0.18eV$ , respectively.<sup>24</sup> Again, this activation energy is about 1.4eV, which is the same as that for the reactivation of hydrogen-shallow-impurity complexes.

(3) With the forward-biased injection of minority carriers into Schottky diodes, Tavendale et al. detected rapid reactivation of hydrogen-boron complexes at 300K.<sup>6</sup> They also showed that a drastic reduction in neutralization of boron acceptors under white light illumination.<sup>25</sup>

In view of these results, we now point out the deficiencies of the intuitive model of reactivation. According to this model, the reactivation of impurities is due to the dissociation of hydrogen from the hydrogen-impurity complexes directly. Since the binding energies for hydrogen-acceptor and hydrogen-donor complexes are quite different, it is expected that the corresponding activation energies will show large variation which is inconsistent with what has been observed. Furthermore, it is very difficult to visualize that under the condition of injection of minority carriers and white light illumination the dissociation rate can be enhanced rapidly. At least, there has no reports giving a satisfactory interpretation. Thus, we believe that reconsideration of the reactivation mechanism of hydrogen-impurity complexes in crystalline silicon is needed.

We now seek a possible mechanism to explain the experimental results described above. The atomic structure change induced by carrier injection or light illumination are reminiscent of the metastability in hydrogenated amorphous silicon (a-Si:H). In a-Si:H, the light induced degradation is known as the Staebler-Wronski effect<sup>26</sup> and has been studied extensively. A correct description of the reactivation of hydrogen-impurity complexes in crystalline silicon may enhance our understanding of the technologically important Staebler-Wronski effect in a-Si:H.

Since the dissociation of hydrogen from a hydrogen-impurity complex does not depend on dopant species, we propose that the breaking of hydrogen-passivating bonds is

due to an isolated atomic hydrogen. This isolated atomic hydrogen and the released hydrogen-shallow from hydrogen-impurity complexes form a hydrogen molecule, and thus the impurity is reactivated. This reaction can be written as



The activation energy of the reactivation therefore reflects the energy needed for the dissociation and diffusion of this isolated atomic hydrogen from a hydrogen-related complex which does not depend on dopant species. There is considerable evidence that atomic hydrogen can readily break bonding in solids. For example, as discussed above atomic hydrogen can break silicon-impurity bonds to form hydrogen-impurity complexes. Sakurai and Hagstrum<sup>27</sup> found that hydrogen atoms could break Si-Si bonds on the (100) surface. Moreover, atomic hydrogen can etch the surface of either amorphous silicon or crystalline silicon to form silane gas molecules.<sup>28</sup> The question right now is what kinds of hydrogen-related complexes can provide this isolated atomic hydrogen. Also, the dissociation rate of hydrogen from this complex can be enhanced by minority carrier injection or light illumination.

As shown from secondary ion mass spectrometry,<sup>1,25</sup> the concentration distribution of deuterium seen in the near-surface region ( $<0.5\mu m$ ) in the deuterated sample can be higher than the actual impurity concentration by more than two order of magnitude. Thus, in hydrogenated samples except forming hydrogen-impurity complexes, it is possible that hydrogen can interact with host atoms and form hydrogen-related complexes. A possible candidate is the diatomic hydrogen complex (denoted by  $H_2^*$ ) proposed by Chang and Chadi.<sup>29</sup> This complex is formed by a neutral hydrogen atom in the bond-centered (BC) site and another in an adjacent tetrahedral site ( $T_d$ ) near the antibonding site (see Ref. 29). The hydrogen atoms break the Si-Si bond and form Si-H bonds with stretching frequencies at  $2070\text{ cm}^{-1}$  and  $1480\text{ cm}^{-1}$  for hydrogen in the BC and  $T_d$  sites, respectively. This pair can roughly be viewed as an intimate association of the charge defects  $H^+(BC)$  and  $H^-(T_d)$  which because of close proximity are lower in energy. In the process of forming, the intimate association of the charge is transferred by making both H atoms approximately charge neutral. This  $H_2^*$  complex is lower in energy than most other configurations except Si-H at a vacancy or an  $H^+$  in a BC site in strongly p-type silicon. Thus, it is possible that this  $H_2^*$  complex can exist in hydrogenated crystalline and amorphous silicon. Indeed, Jackson<sup>30</sup> has recently applied this complex to explain the metastability of a-Si:H. It is claimed that a large body of experimental facts is consistent with the proposed model.

Here, we will adapt this  $H_2^*$  complex to explain the reactivation of shallow impurity in hydrogenated crystalline silicon. It is proposed that the reactivation occurs when this complex dissociates either thermally or through carriers induced by light illumination or injection into isolated atomic hydrogen configurations which diffuse rapidly to hydrogen-impurity complexes and break hydrogen-impurity bonds. In the case of thermal dissociation, the activation energy for the formation of a hydrogen molecule through this  $H_2^*$  com-

plex is calculated to be  $1.4\text{eV}$ <sup>29</sup> which is in good agreement with the reported value of the activation energy of reactivation of shallow impurities as discussed above. In the case of light illumination or minority carrier injection, the  $H_2^*$  complex is dissociated by trapping electrons and holes in or near the  $H_2^*$  complex. The trapping of carriers occurs because of the fact that the Si-H bond of the  $H_2^*$  complex will reside on one of the Si atoms sharing the weak bond, and carriers created by either the absorption of light or injection are likely to be trapped on weak Si-Si bonds. Since any defect with its mass lighter than that of the surrounding lattice possesses several localized vibrational modes, the energy released from recombinations through the trapped electron-hole pairs will be first converted into the localized vibrational modes of Si-H bonds, then this energy will eventually be able to break the Si-H bonds. The total formation energy surface for hydrogen in BC or  $T_d$  are flat allowing the isolated hydrogen atom dissociated from the  $H_2^*$  complex to readily diffuse apart with an activation energy of  $0.2\text{eV}$  or less.<sup>29</sup> This small activation energy will account for the instability of hydrogen-shallow-impurity complexes under light illumination or minority carrier injection even at room temperature. Thus, our proposed model is able to explain all the experimental facts and can resolve all the deficiencies existing in the intuitive model. The effect discussed here is very similar to the recombination-enhanced defect reaction mechanism studies by Weeks et al.<sup>31</sup> This mechanism involves the non-radiative capture of an electron or hole or both at a defect center via multiphonon recombination. The energy released by the electron-hole pair trapping at a common defect site can be used to reduce the activation energy of the defect reaction, and hence to enhance the reaction rate.

Even the  $H_2^*$  complex can serve as a very good candidate for the reactivation of hydrogen-impurity complexes in crystalline silicon and metastability in amorphous silicon, the evidence for the existence of  $H_2^*$  complex is not clearly found. Chang and Chadi<sup>32</sup> have claimed that the unidentified infrared vibrational mode at  $1660\text{ cm}^{-1}$  observed in hydrogenated n-type silicon could be due to the  $H_2^*$  complex. However, Bergman et al.<sup>13</sup> indicated that this band is sensitive to the chemical identity of the donor and the isotopic substitution ratio of this band increases with the donor mass. They thus suggested that this band involves the donor, hydrogen, and an additional plasma-related defect. Therefore, the experimental signatures of the  $H_2^*$  complex are not conclusive, and further studies are still needed. Although we take the  $H_2^*$  complex to be a good candidate and interpret the experimental results accordingly here, we note that any other hydrogen-related complexes are also possible as long as they can accomplish the following requirements. The activation energy of the dissociation of hydrogen from these complexes is about  $1.4\text{eV}$ . After releasing hydrogen(s), these complexes have to restore to a regular Si-Si bond which does not contain any defects, e.g. dangling bond. Furthermore, these complexes should be able to trap free electron and hole, and hence the dissociation of hydrogen can be enhanced under carrier injection or light illumination.

In conclusion, we have pointed out that a correct mechanism for the reactivation of shallow impurities in hydrogenated crystalline silicon has to explain the facts that the

activation energy of the reactivation does not depend on the type of dopant or dopant species, the reactivation rate can be enhanced under the conditions of light illumination or minority carrier injection. These results can not be interpreted by the currently accepted model which indicates that the reactivation of shallow impurities is the result of the direct dissociation of hydrogen from a hydrogen-impurity complex. We proposed that the breaking of hydrogen-impurity bonds is caused by an isolated atomic hydrogen. The activation energy of the reactivation reflects the energy needed for the dissociation and diffusion of this isolated atomic hydrogen from a hydrogen-related complex which does not depend on dopant species. This hydrogen-related complex releases hydrogen with an activation energy of about 1.4eV, it restores to a regular Si-Si bond after releasing hydrogen, and it can trap free carriers. We also suggested that the diatomic hydrogen complex proposed by Chang and Chadi<sup>29</sup> could be a possible candidate for this hydrogen-related complex. In view of the fact that hydrogen-shallow-impurity complexes in hydrogenated crystalline GaAs also shows instability under light illumination and minority carrier injection,<sup>34</sup> it is possible that the instability of hydrogen-shallow-impurity complexes occurs in all hydrogenated semiconductors. Thus, the understanding of reactivation of hydrogen-shallow-impurity complexes is fundamentally and technologically important.

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