RESEARCH BULLETIN OF THE
HIROSHIMA INSTITUTE OF TECH.
VOL. 33 (1999) PP. 19-24

P A P E R

Model of the Light-Induced Defect Creation in Hydrogenated Amorphous Silicon

Kazuo MORIGAKI*

(Received Sept. 30, 1998)

Abstract

A previous model that prolonged illumination creates two types of dangling bonds, i.e., normal dangling bonds and hydrogen-related dangling bonds (dangling bonds having hydrogen at a nearby site) is modified by taking into account recent observations in a-Si:H, particularly on diffusion of hydrogen dissociated from a Si-H bond by nonradiative recombination at hydrogen-related dangling bonds and intradistance within a close pair of two types of dangling bonds.

1. Introduction

The light-induced creation of dangling bonds in hydrogenated amorphous silicon (a-Si:H) results in the degradation of amorphous silicon solar cells that is the most important issue for development of high-efficiency amorphous silicon solar cells[1]. It has been known that this light-induced degradation in a-Si:H is caused by the light-induced creation of dangling bonds since the first ESR measurements by Hirabayashi et al.[2] and by Dersch et al.[3]. However, the origin of the light-induced creation of dangling bonds in a-Si:H is still unclear and a controversial issue. Since I proposed a microscopic model for light-induced creation of dangling bonds in a-Si:H a decade ago[4,5], many information has been accumulated on this issue. So, in this paper, I present a modified model by taking into account the recent experimental results on the light-induced creation of dangling bonds in this material.

One of the most important conclusion of a previous model[4,5] is the presence of dangling bonds having hydrogen at a nearby site (hydrogen-related dangling bonds). This has been confirmed from the ENDOR (electron nuclear double resonance) measurement on a-Si:H[6] and a-Si:D[7] samples containing a large amount of hydrogen and deuterium, respectively. For high-quality a-Si:H samples, there is no direct evidence for the presence of hydrogen-related dangling bonds, because the sensitivity of detection of ENDOR signals is limited not enough to detect them for these samples owing to a small number of their dangling bonds. Deconvolution of the dangling-bond ESR spectra into two components due to two types of dangling bonds[8,9], i.e., normal dangling bonds and hydrogen-related dangling bonds provides an indirect means to identify them. Our recent investigations[10] on deconvolution suggest that this is the case even for high-quality a-Si:H samples as well as for low-quality samples containing a large amount of hydrogen and dangling bonds. A previous model[4,5] for the light-induced defect creation leads us to the creation of equal number of two types of dangling bonds by prolonged illumination. The previous deconvolution[8] showed that this is the case for a-Si:H samples prepared at 100°C containing a large amount of hydrogen (hydrogen content [H]≅20 at.%). The ENDOR measurements[6], support this conclusion. In the previous model, it was assumed that two types of dangling bonds are separated by 6–7Å. Our recent study[10] suggests that mutual distance within a close pair of two types of dangling bonds is about 13Å. The distance should be distributed, so that this dis-

* Department of Electrical Engineering, Faculty of Engineering, Hiroshima Institute of Technology

tance corresponds to an average distance. In this paper, the model is extended to take into account this result. Furthermore, the light-induced annealing of dangling bonds[11,12] is also taken into account. It will be also pointed out that normal dangling bonds may be photocreated more than hydrogen-related dangling bonds.

For the viewpoint of a modified model for the light-induced defect creation, attention is paid for two recent proposals, i.e., one of them is that by Godet and Roca i Cabarrocas[13], i.e., recombination of an electron and a hole at two closed Si-H bonds creates a three-centre bond, Si-H-Si and that dangling bonds are created from these three-centre bonds. The other is that by Branz[14], i.e., the process of light-induced creation of a normal dangling bond and a hydrogen-related dangling bond (he called it Si-H/dangling bond complex) is similar to a previous model, but two hydrogen-related dangling bonds collide with each other and then normal dangling bonds are left behind, so that the light-induced defects are only normal dangling bonds. In his model, the rate-limiting process of light-induced defect creation is the collison process mentioned above.

2. Light-induced defect creation processes

The previous model of the light-induced defect creation is based on the breaking of specific weak Si-Si bonds, as shown in Fig. 1(a), which was first suggested by Hirabayashi et al.[2]. The model consists of the following three processes: (1) Self-trapping of a hole in a specific weak Si-Si bond, i.e., a Si-Si bond adjacent to a Si-H bond. Nonradiative recombination occurs between an electron and this hole at this weak bond. (2) Switching of the Si-H bond towards the weak Si-Si bond before or simultaneously when an electron recombines with a hole in the weak Si-Si bond. (3) Hopping and/or tunneling of hydrogen into another site along the weak Si-Si bond. These processes are repeated for further movement of the created dangling bond site. When hydrogen moves to another site where it is bonded to a Si atom, the Si-Si bond adjacent to this new Si-H bond becomes weak, and then this weak Si-Si bond will be broken when a hole is self-trapped at this bond, followed by nonradiative recombination at this bond. Then, two separate dangling bonds, i.e., a normal dangling bond and a hydrogen-related dangling bond, are created, as shown in Fig. 1(c). The light-induced creation rate of two separate dangling bonds R_C and creation efficiency C_{SW} were calculated[4,5], taking into account these processes. The magnitude of R_C and its temperature dependence were in good agreement with the observations. In the configuration shown in Fig. 1(c), however, the distance between two separate dangling bonds ranges between 6 and 7Å, taking into account the flexible structure of the amorphous network. This distance is smaller than the value of 13Å which was suggested from an analysis[10] of the spin-packet width of the dangling-bond ESR line observed by Brandt et al.[15] at 434 MHz.

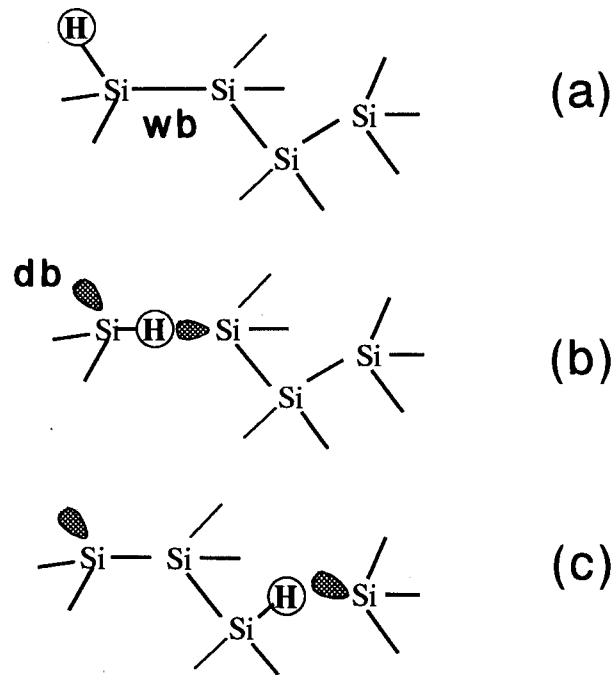

Fig. 1 Atomic configurations corresponding to the initial step (before illumination) (a), the intermediate step (b), and the final step (c) during illumination; wb, weak bond; db, dangling bond.

In the following, the configuration shown in Fig. 2 is considered. For the light-induced creation of two types of dangling bonds shown in this configuration, the value of C_{SW} is decreased with a factor of 2×10^{-2} at room temperature compared to the configuration shown in Fig. 1(c). The light-induced dangling bond density ΔN_S for ESR mea-

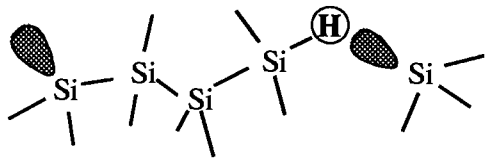

Fig. 2 Atomic configuration of separate dangling bonds.

surements by Stutzmann et al.[16] is estimated as follows: They used prolonged illumination of Kr^+ laser light at 1.91 eV with 400 mW/cm^2 for 30 min at room temperature. The observed value of ΔN_S is 2.6×10^{16} cm^{-3}. The estimated value of DNS is 1.6×10^{16} cm^{-3}, using a calculated value of C_{SW} ($C_{SW}=1.03 \times 10^{-8}$) which is obtained by taking into account its temperature dependence with activation energy observed by Stutzmann et al[16]. Thus, this estimated value is also consistent with the observed one, but the distance between two separate dangling bonds that is 9–10Å is still longer than 13Å. Then, further consideration is required to find processes for two types of dangling bonds to separate with each other.

In the following, a modified model is presented for light-induced creation of two types of dangling bonds. Very recently, we have observed that the light-induced annealing process predominates over the light-induced creation process in a-Si:H samples containing a large amount of hydrogen[11,12]. It was pointed out that nonradiative recombination at hydrogen-related dangling bonds followed by dissociation of hydrogen plays an important role in the light-induced annealing of dangling bonds in a-Si:H. Both the light-induced creation and annealing processes are taken into account. Hydrogen dissociated from a hydrogen-related dangling bond has two main possibilities: One of them is that it terminates a normal dangling bond created as a partner of a closed pair of dangling bonds, as shown in Figs. 3(a) and (b). The other is that it inserts into a neighboring Si-Si bond to form a Si-H bond and a hydrogen-related dangling bond, as shown in Figs. 3(c) and (d). Thus, these two possibilities are competing with each other. If the distance between a normal dangling bond and a hydrogen-related dangling bond within a closed pair is short

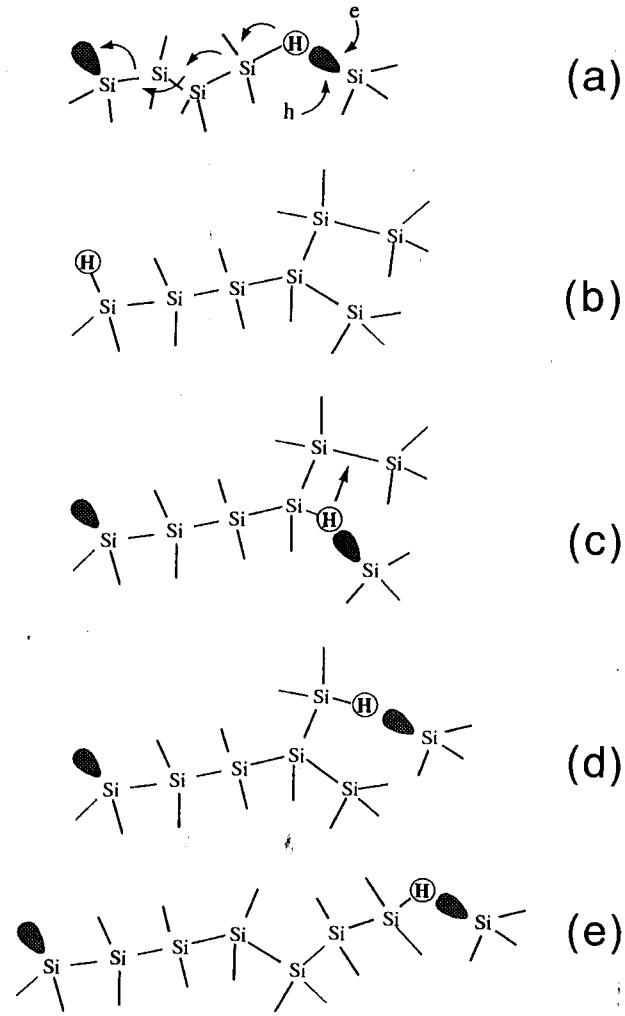

Fig. 3 Atomic configurations corresponding to movement of hydrogen dissociated from a Si-H bond located near a hydrogen-related dangling bond as a result of nonradiative recombination of electrons and holes (a), after termination of a normal dangling bond by hydrogen (b), insertion of hydrogen into a nearby Si-Si bond (c), after insertion of hydrogen into a nearby Si-Si bond (formation of a hydrogen-related dangling bond) (d) and separate dangling bonds (e).

enough to terminate a normal dangling bond compared to the movement of hydrogen to a neighboring Si-Si bond, two types of dangling bonds are annihilated. On the other hand, if the other process predominates over the termination process, the initial hydrogen-related dangling bond is annihilated after dissociation of hydrogen, but a new hydrogen-related dangling bond is created, as shown in Fig. 3(d). Thus, two types of dangling bonds are still left behind. As a result, the mutual distance between a normal dangling

bond and a hydrogen-related dangling bond becomes long, i.e., two type of dangling bonds are more separated with each other compared to their initial separation. The distance between two separate dangling bonds shown in Fig. 3(d) is about 11Å. A configurtion in Fig. 3 (e) gives a distance of about 13Å. The light-induced creation rate of these dangling bonds, however, becomes smaller than those for light-induced creation processes giving rise to the configurations shown in Figs. 1(c) and 2. Quantative consideration should take into account probabilities of dissociation and insertion of hydrogen atoms mentioned above. In this paper, however, discussion is limited to a qualitative one.

The above consideration can be applied to hydrogen-related dangling bonds shown in Fig. 1(b). Then, nonradiative recombination at a hydrogen-related dangling bond causes its nearby hydrogen to be dissociated and then hydrogen inserts into a neighboring Si-Si bond. Repeating these processes, we can reach a configuration shown in Fig. 1(c) or in Fig. 2. Such light-induced creation processes for two types of dangling bonds may be considered as well as the processes mentioned above. It is also pointed out that the light-induced creation and annihilation processes considered above are of dispersive nature, because they occur through the movement of hydrogen, as was previously pointed out[20].

It is also noted that the distance between two separate dangling bonds may be distributed, so that the distance of 13Å is taken as an average value, as mentioned before. Thus, the configurations of two types of dangling bonds considered above are taken into account with some weight.

The rate equations relevant to the above processes are given in Appendix. An important result derived from the rate equations within a framework given above is that the density of light-induced normal dangling bonds is either greater than or equal to that of light-induced hydrogen-related dangling bonds.

In the following, annihilation of hydrogen-related dangling bonds and formation of a coupled pair of Si-H bonds are considered. If hydrogen dissociated from a nearby site of a hydrogen-related dangling bond terminates another hydrogen-related dangling bond, as shown in Figs. 4(a) and (b), then two hydrogen-related dangling bonds are annihilated and, as a result, two normal dangling bonds are left behind, as shown in Fig. 4(c) and (d). This process also gives rise to unbalance in the creation between two types of dangling bonds, i.e., the number of normal dangling bonds exceeds that of hydrogen-related dangling bonds. This process also brings us to create those coupled pairs of Si-H bonds, as shown in Fig. 4(c), which cause an enhancement of the infrared (IR) band at 1940 cm^{-1} and 2060 cm^{-1} by prolonged illumination[17,18]. However, this process occurs when the mutual distance of hydrogen-related dangling bonds is short enough for dissociated hydrogen to diffuse and to terminate one of them. In the following, this process is considered quantitatively. It is assumed that the diffusion coefficient D_H under illumination has a value of 3.2×10^{-19} cm^2/s at room temperature obtained by extraporating the measured value of D_H at higher temperature by Santos et al[19]. The diffusion time of hydrogen over a distance of 3Å and 10Å are estimated to be 47 min and 8.7 h, respectively. This result suggests that the mutual distance between two-hydrogen-related dangling bonds is required to be

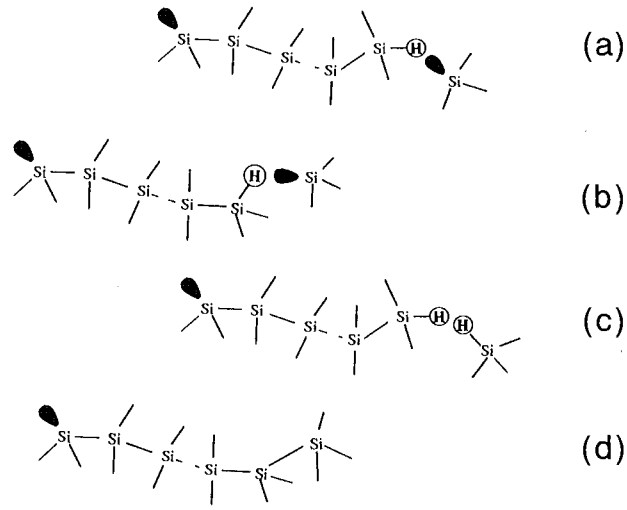

Fig. 4 Atomic configurations corresponding to before (a), (b) and after (c), (d) termination of a hydrogen-related dangling bonds by hydrogen dissociated from a Si-H located near other hydrogen-related dangling bond.

so short as 3Å in order for the above process to occur. This may be only the case for a-Si:H samples containing a large amount of hydrogen in which dangling bonds are closely formed and photocreated around voids.

3. Conclusions

The previous model of the light-induced defect creation in a-Si:H is reconsidered by taking into account the recent finding that two types of dangling bonds are separated with average distance of 13Å. In a modified model, the following two processes play an importnt role in separating two types of dangling bonds: dissociation of hydrogen atoms from Si-H bonds located near hydrogen-related dangling bonds as a result of nonradiative recombination of electrons and holes there and insertion of hydrogen atoms into nearby Si-Si bonds. Annihilation of normal dangling bonds and hydrogen-related dangling bonds by diffused hydrogen is also taken into account. A coupled pair of Si-H bonds is also created when two hydrogen-related dangling bonds are close enough for a dissociated hydrogen atom to diffuse and to terminate one of them. In this paper, I discussed these processes qualitatively. A quantitative discussion remains as a future problem.

Appendix

Rate equations relevant to light-induced creation of metastable defects, i.e., normal dangling bonds a and hydrogen-related dangling bonds b, and metastable hydrogen atoms are given as follows:

$$dN_a/dt = C_d np - k_2 N_m N_a, \quad \text{(A1)}$$

$$dN_b/dt = C_d np - k_1 N_b + k_3 N_m N_{Si} - k_4 N_m N_b, \quad \text{(A2)}$$

$$dN_m/dt = k_1 N_b - k_2 N_m N_a - k_3 N_m N_{Si} - k_4 N_m N_b, \quad \text{(A3)}$$

where N_a, N_b, N_m, N_{Si}, n, and p are densities of normal dangling bonds, hydrogen-related dangling bonds, metastable hydrogen atoms, silicon atoms, free electrons and free holes, respectively, and C_d, k_1, k_2, k_3, and k_4 are coefficients of light-induced creation reaction of two types of dangling bonds, dissociation reaction of hydrogen atoms from Si-H bonds located near hydrogen-related dangling bonds, termination reaction of normal dangling bonds by metastable hydrogen atoms, insertion reaction of metastable hydrogen atoms into Si-Si bonds, and termination reaction of hydrogen-related dangling bonds by metastable hydrogen atoms, respectively.

First, we consider the steady state in the case of $k_4=0$. Then, we obtain a relationship among N_a, N_b, and N_m as follows:

$$N_a - N_b = N_m, \quad \text{(A4)}$$

Equation (A4) indicates $N_a \geqq N_b$.

We resolve the following equations to obtain N_a and N_b:

$$N_a = C_d np/k_2 N_m, \quad \text{(A5)}$$

$$N_b = (C_d np + k_3 N_m N_{Si})/k_1, \quad \text{(A6)}$$

For $k_3=0$, we obtain

$$N_a = (C_d np/2k_1)[1+\sqrt{1+4(k_1^2/C_d np\, k_2)}], \quad \text{(A7)}$$

$$N_b = C_d np/k_1, \quad \text{(A8)}$$

For $k_3 \neq 0$, we obtain

$$N_a = (C_d np/2k_1)[1+\sqrt{1+4\, k_1(k_4+k_3 N_{Si})/C_d np\, k_2}], \quad \text{(A9)}$$

$$N_b = (C_d np + k_3 N_{Si} N_a)/(k_1 + k_3 N_{Si}), \quad \text{(A10)}$$

Secondly, we consider the case of $k_4 \neq 0$. In this case, we cannot reach the steady state. A detailed account of the appendix will be given elsewhere.

References

1) D.L. Staebler and C.R. Wronski: Appl. Phys. Lett. 31 (1977) 292.
2) I. Hirabayashi, K. Morigaki and S. Nitta: Jpn. J. Appl. Phys. 19 (1980) L357.
3) H. Dersch, J. Stuke and J. Beichler: Appl. Phys. Lett. 38 (1981) 456.
4) K. Morigaki: Jpn. J. Appl. Phys. 27 (1988) 163.
5) K. Morigaki: J. Non-Cryst. Solids 141 (1992) 166.
6) H. Yokomichi and K. Morigaki: Solid State Commun. 63 (1987) 629.
7) H. Yokomichi and K. Morigaki: Philos. Mag. Lett. 73 (1996) 283.
8) H. Hikita, K. Takeda, Y. Kimura, H. Yokomichi and K. Morigaki: J. Phys. Soc. Japan 66 (1997) 1730.
9) K. Morigaki, H. Hikita, M. Yamaguchi and Y.

Fujita: J. Non-Cryst. Solids 227–230 (1998) 338.
10) K. Morigaki and H. Hikita: This issue.
11) K. Takeda, H. Hikita, Y. Kimura, H. Yokomichi, M. Yamaguchi and K. Morigaki: Jpn. J. Appl. Phys. 36 (1997) 991.
12) K. Takeda, H. Hikita, A. Kondo, A. Ganjoo, K. Shimakawa and K. Morigaki: J. Non-Cryst. Solids 227–230 (1998) 311.
13) C. Godet and P. Roca i Cabarrocas: J. Appl. Phys. 80 (1996) 97.
14) H.M. Branz: Solid State Commun. 105 (1998) 387.
15) M.S. Brandt, M.W. Bayerl, M. Stutzmann and C.F.O. Graeff: J. Non-Cryst. Solids 227–230 (1998) 343.
16) M. Stutzmann, W.B. Jackson and C.C. Tsai: Phys. Rev. B32 (1985) 23.
17) Y. Zhao, D. Zhang, G. Kong, G. Pan and X. Liao: Phys. Rev. Lett. 74 (1995) 558.
18) K. Morigaki: Kotai Butsuri (Solid State Physics) 33 (1998) 157.
19) P.V. Santos, N.M. Johnson and R.A. Street: Phys. Rev. Lett. 67 (1991) 2686.
20) K. Morigaki and F. Yonezawa: J. Non-Cryst. Solids 164–166 (1993) 215.