# Fast Diffusion of H and Creation of Dangling Bonds in Hydrogenated Amorphous Silicon Studied by *in situ* ESR

U. K. Das,* T. Yasuda, and S. Yamasaki

*Joint Research Center for Atom Technology, 1-1-4 Higashi, Tsukuba, Ibaraki 305 0046, Japan*

(Received 2 February 2000)

The interaction of atomic hydrogen with *a*-Si:H films was studied by means of *in situ* ESR during H plasma treatment. H diffuses into the *a*-Si:H film and creates additional Si dangling bonds ($\sim 10^{13}\ \mathrm{cm}^{-2}$). We observed a high diffusion coefficient ($>10^{-10}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$) at the very initial stage of H treatment (<1 s). The resulting additional dangling bonds are spatially distributed (~100 nm) into the bulk film. The characteristic depth of dangling bond (db) distribution decreases with increasing H treatment temperature. The activated rate constants of db creation and annihilation reactions determine the distribution of additional dangling bonds at different treatment temperatures.

PACS numbers: 61.43.Dq, 52.75.Rx, 66.30.Ny, 76.30.–v

The high mobility and amphoteric nature of hydrogen and its isotopes have long been verified to play a key role in modifying the optical and electrical properties of various semiconductors such as crystalline Si, polycrystalline Si, and hydrogenated amorphous Si (*a*-Si:H). H exhibits many intriguing phenomena such as the passivation of shallow impurities in crystalline Si [1,2], $Si/SiO_2$ interface defects to improve the quality of metal-oxide-semiconductor (MOS) transistors [3,4], passivation of grain boundary defects in polycrystalline Si for improving its electrical properties [5], and the passivation of Si dangling bonds (dbs) in *a*-Si:H. Hydrogen reduces the db density from $\sim 10^{19}\ \mathrm{cm}^{-3}$ for *a*-Si to $\sim 10^{15}\ \mathrm{cm}^{-3}$ for device quality *a*-Si:H prepared by the chemical vapor deposition (CVD) method. So studies on the interaction of atomic hydrogen with Si and the dynamic changes of Si matrices are important subjects in various aspects of Si technology. The mechanism of H incorporation and its influence on the microscopic defects of *a*-Si:H films still remains uncertain. The kinetics of the creation, termination, and annihilation of db during *a*-Si:H film growth and $H_2$ plasma treatment have recently been successfully realized by *in situ* ESR studies using remote plasma microwave CVD [6–8]. Our earlier experiments showed that hydrogen creates additional db in *a*-Si:H films during H exposure [8]. Moreover, it was observed that these excess dbs are created not only at the top surface but also at some regions below the surface, unlike the Ar plasma treatment on *a*-Si:H films [8]. In this paper, we addressed two issues: (1) the depth of the distribution of additional dbs [$\Delta n_s(x, t)$, where $x$ is the depth of the *a*-Si:H film and $t$ is the H treatment time] due to H exposure, and (2) the effect of H treatment temperature on the distribution of $\Delta n_s$. The interactions of H with the Si network are discussed based on the experimental results. We found a high diffusion coefficient of H in *a*-Si:H films at the very initial stage of $H_2$ plasma treatment of *a*-Si:H films.

The deposition of *a*-Si:H films and their treatment by a flux of H were carried out using a remote hydrogen plasma as described elsewhere [6,7]. A flow of heated $N_2$ was used to raise the substrate temperature from room temperature to up to 200 °C. The typical experimental conditions were $H_2$ flow rate of 100 SCCM (cubic centimeters per minute at standard temperature and pressure) and $SiH_4$ flow rate of 10 SCCM for deposition. An $H_2$ flow rate of 100 SCCM was used for $H_2$ plasma treatment. Other parameters were the microwave power for sustaining $H_2$ plasma of 50 W and the pressure of ~1.5 Torr. The flux of atomic hydrogen during $H_2$ plasma treatment under the above plasma conditions was estimated to be $\sim 10^{16}\ \mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ from the measurements of gas-phase ESR. To obtain the time evolution of Si dbs, the magnetic field for ESR was set at the peak position of the first derivative spectrum due to Si dbs.

To realize the spatial distribution of dbs in *a*-Si:H films during H treatment, we performed a thickness dependence study of H treatment at different temperatures. If the dbs are created only at the film surface, the resulting additional dbs [i.e., the total dbs created in the film of thickness $d$ due to H exposure; $\Delta N_s = \int_0^d \Delta n_s(x, \infty)\, dx$, where $\Delta n_s(x, \infty)$ denotes the value of the equilibrated $\Delta n_s$ at film depth $x$] will be independent of film thickness. Otherwise, in the case of some spatial distribution of dbs in the deeper regions, $\Delta N_s$ should increase with the film thickness. H plasma treatment for 3 min was repeated after each deposition (namely, at each film thickness). We did not observe any significant etching of *a*-Si:H film during 3 min of H treatment under our plasma conditions. The values of $\Delta N_s$ at each film thickness were obtained by averaging 1024 data procured during 84 s. The interval of 15 min between each deposition and H treatment was maintained constant. Also, we performed separate deposition and subsequent H treatment to check for any influence of the repeated deposition and H treatment on the $\Delta N_s$ value, but the $\Delta N_s$ value was almost the same in both cases.

Figure 1 shows the variation of $\Delta N_s$ as a function of film thickness for the *a*-Si:H films treated at 120 °C and 150 °C. The deposition temperature ($T_d$) was the same as the plasma treatment temperature ($T_p$). The figure shows

 0031-9007/00/85(11)/2324(4)$15.00 

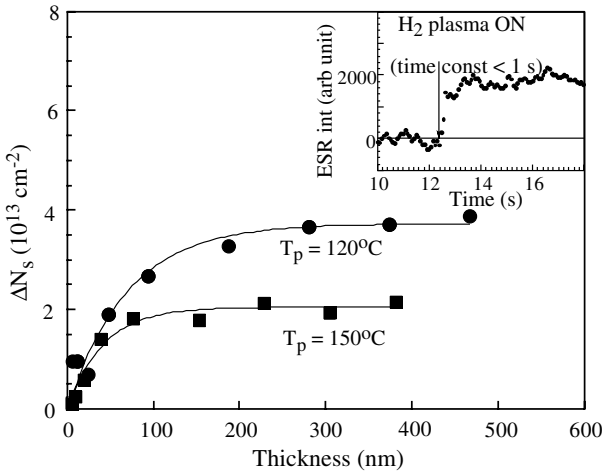


FIG. 1. Variation of total additional dbs ($\Delta N_s$) created in the $a$-Si:H films due to H exposure as a function of film thickness at treatment temperatures of 120 °C and 150 °C (note that the deposition temperature was the same as the treatment temperature). The inset shows a typical time evolution of ESR intensity at the very initial stage of H treatment at 150 °C.

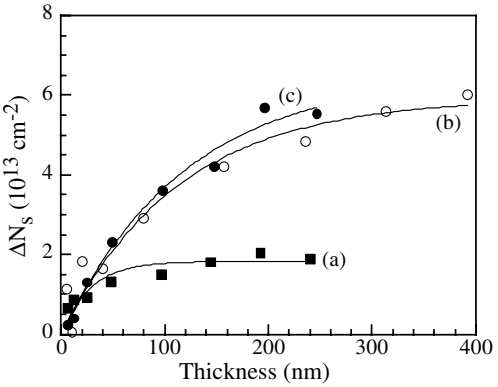


FIG. 2. Thickness dependence of $\Delta N_s$ for the three different deposition and treatment temperatures: ($a$) deposition temperature ($T_d$) of 200 °C, H treatment temperature ($T_p$) of 200 °C, ($b$) $T_d$ of 100 °C, $T_p$ of 100 °C, and ($c$) $T_d$ of 200 °C, $T_p$ of 100 °C.

that $\Delta N_s$ saturates at a film thickness of ~100 nm. The inset of Fig. 1 shows a typical time evolution of Si db signal at 150 °C. A rapid increase of ESR intensity (with time constant <1 s) followed by the saturation of ESR signal is observed during H exposure to the $a$-Si:H film. It is worth mentioning here that we did not observe $\Delta N_s$ at the temperatures below 80 °C in our present experimental condition, because the relaxation of dbs after deposition becomes slower at lower temperature [9]. The large number of dbs, which remain even after 15 min from the deposition off time, masks the creation of additional db due to H exposure.

The different amount of $\Delta N_s$ at different treatment temperatures (Fig. 1) may be argued to be an effect of different film structure caused by the different $T_d$ and not an effect of $T_p$. In order to check the effect of film structure on the $\Delta n_s$ distribution, we deposited a film at 200 °C ($T_d$) and treated it by H at 100 °C ($T_p$). The data are compared with the films treated by H at the same temperature of deposition (viz. $T_d, T_p$ = 200 °C and $T_d, T_p$ = 100 °C) in Fig. 2. The figure shows that the data of $T_d$ = 200 °C, $T_p$ = 100 °C [curve ($c$)] closely resemble the data of $T_d$ = 100 °C, $T_p$ = 100 °C [curve ($b$)]. Therefore, we conclude that the possible change in film structure due to different $T_d$ has a negligible effect on $\Delta N_s$ in the temperature range of 80 °C–200 °C.

Primarily, an H atom can create a db in $a$-Si:H films by a number of competitive processes:

(i) Creation of dangling bonds:

$$\mathrm{H} + \equiv\mathrm{Si\text{-}Si}\equiv(\mathrm{s}) \rightarrow \mathrm{H\text{-}Si}\equiv(\mathrm{s}) + \equiv\mathrm{Si\text{-}(s)}\,, \quad (1)$$

$$\mathrm{H} + \equiv\mathrm{Si\text{-}H(s)} \rightarrow \mathrm{H_2(g)} + \equiv\mathrm{Si\text{-}(s)}\,. \quad (2)$$

(ii) Termination of dangling bonds:

$$\mathrm{H} + \equiv\mathrm{Si\text{-}(s)} \rightarrow \equiv\mathrm{Si\text{-}H(s)}\,, \quad (3)$$

where (g), (s), H, and ≡ Si-(s) denote the "gas phase," "solid phase," free hydrogen, and a Si db, respectively.

(iii) The annihilation of two nearby dbs primarily due to the thermal reconstruction, albeit not directly related to the interaction of H, contributes to the value of $\Delta N_s$:

$$\equiv\mathrm{Si\text{-}(s)} + -\mathrm{Si}\equiv(\mathrm{s}) \rightarrow \equiv\mathrm{Si\text{-}Si}\equiv(\mathrm{s})\,. \quad (4)$$

(iv) The $H_2$ effusion from two nearby Si-H, although it does not control the evolution of db, is also an important process for stabilizing the $a$-Si:H matrix [10]:

$$\equiv\mathrm{Si\text{-}H(s)} + \mathrm{H\text{-}Si}\equiv(\mathrm{s}) \rightarrow \equiv\mathrm{Si\text{-}Si}\equiv(\mathrm{s}) + \mathrm{H_2}\,. \quad (5)$$

A net increase in the ESR intensity during H treatment (inset of Fig. 1) suggests that processes (1) and (2) dominate over processes (3) and (4) during H exposure to the $a$-Si:H films. Relaxation processes (4) and (5) are strongly dependent on $T_p$ and the rate of relaxation processes (4) and (5) increases with $T_p$ as observed after switching off the plasma [9]. Process (5) should have a large influence on equilibrating the H concentration in the film during H treatment and on determining the amount of bonded H in the film after H treatment.

The spatiotemporal variation of additional dbs $[\Delta n_s(x,t)]$ due to the in-diffusion of H can be described as follows. The densities of ≡Si-Si≡ and ≡Si-H are considerably larger than the concentration of free H ($H_f$) and Si dbs. Thus we can consider these densities as constants. The $H_f$ diminishes as H diffuses from the surface into the bulk due to the reactions (1)–(3). The rate of change of $H_f(x,t)$ and the variation of $\Delta n_s(x,t)$ due to the reactions (1)–(4) can be simultaneously expressed as

$$\frac{\partial H_f}{\partial t} = D_f \frac{\partial^2 H_f}{\partial x^2} - H_f[k_1 N_{\text{Si-Si}} + k_2 N_{\text{Si-H}} + k_3 \Delta n_s] \tag{6}$$

and

$$\frac{\partial \Delta n_s}{\partial t} = H_f[k_1 N_{\text{Si-Si}} + k_2 N_{\text{Si-H}} - k_3 \Delta n_s] - 2k_4(\Delta n_s)^2, \tag{7}$$

where $D_f$ and $x$ are the diffusion coefficient of free H and the depth of film from the surface, respectively; $k_1$, $k_2$, $k_3$, and $k_4$ are the reaction rates of processes (1), (2), (3), and (4), respectively; $N_{\text{Si-Si}}$ and $N_{\text{Si-H}}$ are the concentrations of ≡Si-Si≡ and ≡Si-H, respectively. We tentatively assume that the square term of Eq. (7) describes the annihilation of two dbs due to thermal reconstruction. At steady state, $\partial H_f/\partial t = \partial \Delta n_s/\partial t = 0$. Now we can categorize two regions.

*Region I.*—(Near the vicinity of film surface): When $H_f(x)$ is large, the rates of reactions (1)–(3) are large and therefore the annihilation of two nearby dbs will be negligible. So $\Delta n_s$ will be independent of $H_f$ [$\Delta n_s = (k_1 N_{\text{Si-Si}} + k_2 N_{\text{Si-H}})/k_3$ from Eq. (7)]. Therefore, $\Delta N_s$ will increase linearly with the depth of the film ($x$) in the vicinity of film surface (low $x$ region), and $H_f$ will diminish exponentially from the surface [from Eq. (6)].

*Region II.*—(At a finite depth of the film): When the db creation and termination term in Eq. (7) becomes comparable to the db annihilation term, the $\Delta n_s$ distribution will be much more complicated. Assuming $\Delta n_s$ decays exponentially from the top film surface, the reasonable fits of the experimental data are obtained (solid lines in Figs. 1 and 2) using

$$\Delta N_s = (\Delta N_s)_{\text{sat}}[1 - \exp(-d/\lambda)], \tag{8}$$

where $(\Delta N_s)_{\text{sat}}$ is a constant that depends on the $T_p$, $d$ is the film thickness, and $\lambda$ is the characteristic depth of the $\Delta n_s$ distribution and can be approximated from Eqs. (6) and (7) as

$$\lambda \propto \sqrt{\frac{D_f}{k_1 N_{\text{Si-Si}} + k_2 N_{\text{Si-H}}}}. \tag{9}$$

From the fitting, the characteristic depths of the $\Delta n_s$ distribution ($\lambda$) are estimated and plotted as a function of $T_p$ in Fig. 3. The depth of dangling bond distribution is very sensitive to $T_p$, which reduces with increasing H treatment temperature (Fig. 3). Thus, from Eq. (9) and Fig. 3 we conclude that either or both of $k_1$ and $k_2$ are more strongly activated than $D_f$. We estimated the difference $(\Delta E_k - \Delta E_D)$ of activation energies for the rate constants of db creation ($\Delta E_k$) and for the free H diffusion coefficient ($\Delta E_D$) using Eq. (9). The inset of Fig. 3 shows the variation of $1/\lambda^2$ as a function of $1000/T_p$. The fitting of the curve to an exponential function gives an estimate of $(\Delta E_k - \Delta E_D)$ as ~0.4 eV. The increase of rate constants for the db creation reactions at higher $T_p$ result in

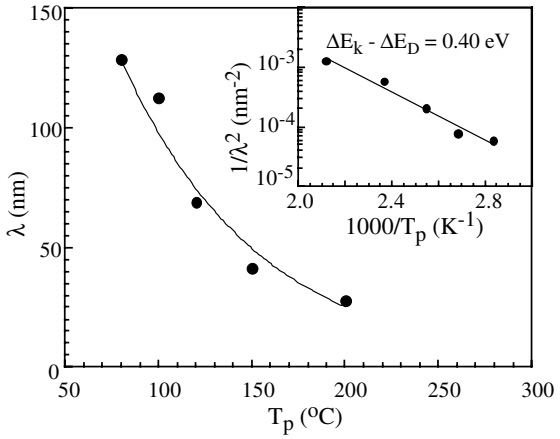


FIG. 3. Variation of characteristic depth of db distribution ($\lambda$) as a function of treatment temperature ($T_p$). The inset shows the Arrhenius plot for $1/\lambda^2$. The activation energy is the resultant of the activation energy for db creation ($\Delta E_k$) and the activation energy of free H diffusion coefficient ($\Delta E_D$).

the higher trap density of free H and formation of db closer to the film surface. The process thereby shortens the $\Delta n_s$ distribution at higher temperatures. Also, the values of $\Delta N_s$ will be higher at the near-surface region (Region I) at higher $T_p$. However, our present ESR signal-to-noise ratio for a small film thickness (~10 nm) is not enough to discuss the rate of initial increase of $\Delta N_s$.

The thickness dependence of $\Delta N_s$ (Fig. 1) suggests that H diffuses into some depth (~100 nm) of the $a$-Si:H film and results in an additional dbs (with time constant <1 s) according to processes (1)–(4). Therefore, considering the fast saturation of dbs (time constant <1 s) during H treatment (inset of Fig. 1) and the $\Delta N_s$ distribution of ~100 nm, the diffusion coefficient of free H ($D_f$) appears to be larger than $10^{-10}$ cm$^2$ s$^{-1}$ [$L = (D_f t)^{1/2}$, where $L$ is the diffusing distance and $t$ is the diffusing time]. This result is in contrast with the usual activated type of H diffusion in $a$-Si:H films observed by thermal/plasma treatment and secondary ion mass spectroscopy (SIMS) [11–13].

The effective diffusion coefficient of H is expected to reduce after the initial creation of a large number of dbs, because the $\Delta n_s$ created (time constant <1 s) in the vicinity of the film surface will then act as the trapping center for H. Beyer *et al.* observed a low value of effective deuterium diffusion coefficient ($D_{\text{eff}} \sim 10^{-15}$ cm$^2$ s$^{-1}$) in $a$-Si:H films after 2 h of deuterium plasma treatment at 250 °C with a diffusion activation energy of 0.77 eV at low temperature range (<400 °C) [13]. For a long H treatment time (~1 h), a small amount of H can permeate deep into the film, which is enough to make a steady state between the annihilation term of Eq. (4) and the creation term of Eqs. (1) and (2) to maintain the deep db distribution in the film [Region II]. This is reasonable because the $\Delta N_s$ created by H treatment (~$10^{18}$ cm$^{-3}$ for 100 nm of $a$-Si:H film) is much less than the incorporated H

($>10^{20}$ cm$^{-3}$ as observed by SIMS even for 10 s deuterium plasma treatment). The details of our SIMS experiment will be reported elsewhere.

Therefore, considering all the above experimental results, we distinguish two different steps in which H interacts with the $a$-Si:H matrix. In step 1, free H diffuses very fast ($D_f > 10^{-10}$ cm$^2$ s$^{-1}$) into the film and creates dbs during in-diffusion by reacting with the Si:H network according to processes (1)–(4). Such a high diffusion coefficient ($>10^{-10}$ cm$^2$ s$^{-1}$) of H is indeed reported in crystalline Si [14]. In step II, after the creation of dbs within a short time ($<1$ s), the diffusion coefficient of H decreases drastically due to the presence of a large number of dbs. Then the H diffuses with $D_{\text{eff}} < 10^{-14}$ cm$^2$ s$^{-1}$ through the modified network following the usual H diffusion processes explained elsewhere [11–13].

The fast diffusion of H and the creation of dbs in $a$-Si:H films may have a correlation with the light induced degradation processes in $a$-Si:H, since the motion of atomic H is assumed to be responsible for light induced degradation in various models [15,16]. In fact, Branz speculated such a high diffusion coefficient ($\sim 10^{-7}$ cm$^2$ s$^{-1}$) of mobile H to explain the metastable degradation of $a$-Si:H films by pulsed illumination [17].

In conclusion, we observed a remarkably high diffusion coefficient ($D_f > 10^{-10}$ cm$^2$ s$^{-1}$) of atomic H in $a$-Si:H films during H treatment. At the very initial stage ($<1$ s), the fast diffusion of H results in additional dbs that are spatially distributed in the bulk ($\sim 100$ nm) of $a$-Si:H films. Such a fast diffusion of free H is a self-limiting process as dbs created near the surface (in $<1$ s) act as a trapping center of the impinging H. Consequently, the effective diffusion coefficient of H reduces drastically ($D_{\text{eff}} < 10^{-14}$ cm$^2$ s$^{-1}$) for longer treatment. Such a low diffusion coefficient of H in $a$-Si:H films has usually been observed in SIMS depth profile studies [11–13]. The depth of db distribution due to the fast diffusion of H reduces with the increase of treatment temperature. An activated type of rate constant for the creation of dbs determines the spatial distribution of dbs.

The authors are grateful to Professor K. Tanaka, Dr. S. D. Baranovskii, and Dr. John Robertson for their encouragement and valuable comments on the paper. The work, which is partly supported by NEDO, was performed in the Joint Research Center for Atom Technology (JRCAT) under the joint research agreement between the National Institute for Advanced Interdisciplinary Research (NAIR) and the Angstrom Technology Partnership (ATP).

*Email address: ukdas@jrcat.or.jp

[1] J. I. Pankove, D. E. Carlson, J. E. Berkheiser, and R. O. Wance, Phys. Rev. Lett. **51**, 2224 (1983).
[2] N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. **56**, 769 (1986).
[3] J. W. Lyding, K. Hess, and I. C. Kizilyalli, Appl. Phys. Lett. **68**, 2526 (1996).
[4] P. J. Chen and R. M. Wallace, Mater. Res. Soc. Symp. Proc. **513**, 325 (1998).
[5] C. H. Seager and D. S. Ginley, Appl. Phys. Lett. **34**, 337 (1979).
[6] S. Yamasaki, T. Umeda, J. Isoya, and K. Tanaka, Appl. Phys. Lett. **70**, 1137 (1997).
[7] S. Yamasaki, T. Umeda, J. Isoya, and K. Tanaka, J. Non-Cryst. Solids **227–230**, 83 (1998).
[8] S. Yamasaki, C. Malten, T. Umeda, J. Isoya, and K. Tanaka, Mater. Res. Soc. Symp. Proc. **536**, 463 (1999).
[9] S. Yamasaki, U. K. Das, T. Umeda, J. Isoya, and K. Tanaka, in *Proceedings of the Eighteenth International Conference on Amorphous and Microcrystalline Semiconductors—Science and Technology, Snowbird, Utah, 1999,* (Elsevier, Amsterdam, 2000).
[10] J. Robertson, J. Appl. Phys. **87**, 2608 (2000).
[11] W. B. Jackson and C. C. Tsai, Phys. Rev. B **45**, 6564 (1992).
[12] W. Beyer and H. Wagner, Mater. Res. Soc. Symp. Proc. **336**, 323 (1994).
[13] W. Beyer and U. Zastrow, Mater. Res. Soc. Symp. Proc. **420**, 497 (1996).
[14] S. J. Pearton, J. W. Corbett, and J. T. Borenstein, Physica (Amsterdam) **170B**, 85 (1991).
[15] R. Biswas and Y. P. Li, Phys. Rev. Lett. **82**, 2512 (1999).
[16] H. M. Branz, Phys. Rev. B **59**, 5498 (1999).
[17] H. M. Branz, Phys. Rev. B **60**, 7725 (1999).