Light-induced annealing of dangling bonds in He-diluted glow discharge a-Si:H films

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Abstract

We report the results of a study of light-induced annealing of dangling bonds, as well as their light-induced creation in He-diluted glow discharge a-Si:H with a large amount of hydrogen at room temperature RT and at 75°C, by using an electron spin resonance (ESR) technique. Under illumination 0.7 W/cm² at room temperature, dangling bonds are created by prolonged illumination, and their density tends to saturate. On the other hand, under strong illumination (1.6 W/cm²) at room temperature, dangling bonds are initially created and then photoannealed after 5 min of illumination. These results for He-diluted glow discharge samples are discussed and compared with those for standard and H₂-diluted glow discharge samples. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Light-induced annealing; Dangling bond; He-diluted glow discharge a-Si:H film; Electron spin resonance (ESR); Illumination

1. Introduction

Very recently, we obtained direct evidence for light-induced annealing of dangling bonds in standard and H₂-diluted glow discharge a-Si:H samples from electron spin resonance (ESR) measurements, and proposed a model to account for the observed variation of the dangling-bond density with illumination time [1]. Previous reports concerning light-induced annealing of dangling bonds in a-Si:H are cited in Ref. [1].

In this paper, we present the results of a further study on light-induced annealing of dangling bonds, as well as their light-induced creation in He-diluted glow discharge a-Si:H containing a large amount of hydrogen. The results are discussed by using a previous model [1] in which the location of dangling bonds is divided into the void region and the bulk region. In these two regions, different annealing mechanisms are in effect.

2. Experimental

Samples of a-Si:H used in this study were prepared by using a rf glow discharge method with a gas mixture of He (89.8%) and SiH₄ (10.2%) at a substrate temperature, Tₛ, of 80°C. The hydrogen...
content and the optical gap energy were 36 at.% and 1.95 eV, respectively. Three flake samples (#41-1, #41-2 and #41-3) were taken from the same source deposited on a molybdenum substrate, and were put into the sample tube followed by evacuating at room temperature (RT) for 1 h. Samples #41-1, #41-2 and #41-3 were used for illumination, 0.7 W/cm², at room temperature (RT) and stronger illumination, 1.6 W/cm², at RT and 75°C, respectively.

Light soaking of the samples at RT and 75°C was performed by using a xenon lamp with an IR cut-off filter at 0.7 and 1.6 W/cm². The light soaking was performed on samples put into a quartz tube at RT outside the cavity to achieve homogeneous illumination. For the light soaking at 75°C, sample #41-3 was illuminated inside the cavity, where the sample tube was rotated every 15 min to achieve homogeneous illumination. During light soaking of the samples at RT, the temperature of the samples was 24 to 33°C, depending on light intensity. From this fact, we can see that the temperature increase due to these illuminations is not sufficient for dangling bonds to be thermally annealed.

The dangling-bond density was measured at RT and 75°C by using a conventional X-band ESR spectrometer (JES-FE3X) with 100 kHz magnetic field modulation. The spin density of the dangling bonds, N_b, before illumination was 1.1 × 10¹⁷ cm⁻³.

3. Results

Fig. 1 shows the ESR signal intensity obtained from samples #41-1 and #41-2 normalized to the intensity taken before illumination (I/I₀) as a function of the illumination time for the cases of illumination, 0.7 W/cm², and illumination, 1.6 W/cm², at RT, respectively. In the former case, I/I₀ increases in the initial stage of light soaking, and then remains approximately constant. On the other hand, in the latter case, I/I₀ exhibits a maximum at 5 min of light soaking, then decreases and remains approximately constant. The solid curves in Fig. 1 are the calculated illumination-time dependences of I/I₀ fitted to the experimental points using a rate–equation model which will be described in Section 3.

To investigate the dependence of light-induced metastable change in the defect density on illumination temperature, we performed light soaking at 75°C and 1.6 W/cm², and measured ESR spectra at 75°C for sample #41-3. The dependence of the ESR signal intensity, I, on illumination time for light soaking at 75°C is shown in Fig. 2. The intensity, I, is a maximum after 5 min of light soaking, then decreases and remains approximately constant. The solid curve shows the calculated illumination-time dependence of I fitted to the experimental points using a rate–equation model. It can be seen from Fig. 2 that there is a deviation between the experimental points and the calculated curve for illumination time longer than 5 h.

Next, we attempted to fit a decay part of the experimental points shown in Fig. 2 by a stretched exponential function, I(t) = I(∞) = [I(0) − I(∞)]exp[−(t/τ)β] [2], where I(0) is the ESR signal intensity extrapolated to t = 0, I(∞) is a fitting parameter at t = ∞, τ is a characteristic time, and β is a dispersion parameter. As seen from Fig. 3, the signal intensity due to dangling bonds with time is well-fitted by the stretched exponential function. The obtained fitting parameters β and τ are 0.46 ± 0.06 and (1.93 ± 0.05) × 10³ s, respectively.
Fig. 2. ESR signal intensity, $I$, vs. illumination time for light soaking at 75°C at 1.6 W/cm$^2$ in a-Si:H #41-3. The solid curve is calculated based on the rate-equation model. The values of $a_1$, $b_2$ and $b_3$ in units of h$^{-1}$ in Eqs. (3)-(5) are shown in the figure.

Fig. 4 shows the thermal annealing-time dependence of the ESR signal intensity, $I$, due to dangling bonds created by light soaking at RT (0.7 W/cm$^2$, 11 h) for sample #41-1. By annealing the sample at 75°C, 59% of the light-induced dangling bonds are annealed after 18 h. The annealing behavior of dangling bonds with time is well-fitted by a stretched exponential function. The fitting parameters $\beta$ and $\tau$ are $0.54 \pm 0.05$ and $(5.3 \pm 0.2) \times 10^4$ s, respectively.

4. Discussion

Very recently, we proposed a model to account for light-induced creation and annealing of dangling bonds for standard and H$_2$-diluted glow discharge a-Si:H samples [1]. As seen in Section 3, similar to the results for the standard and H$_2$-diluted glow discharge a-Si:H samples, light-induced creation and annealing of dangling bonds obviously occur for He-diluted glow discharge a-Si:H samples whose relative weight depends on light intensity.

In the following, we attempt to account for the present results using the model proposed in Ref. [1]. The model is outlined below. In our model, the location of dangling bonds is divided into the void region and bulk region. We assume that under illumination, the two processes, (a) and (b), are in effect, namely, (a) dangling bonds located around voids are not photocreared but photoannealed; and (b) dangling bonds in the bulk are photocreared and
photoannealed at the same time. These two processes, (a) and (b), compete with each other. Nonradiative recombination of an electron and a hole at a hydrogen-related dangling bond causes one hydrogen atom or two hydrogen atoms to be dissociated from Si–H or Si–H₂ bonds, with the assistance of emitted hydrogen-related dangling bond causes one hydrogen diative recombination of an electron and a hole at a phonon associated with recombination. These dissociated hydrogen atoms diffuse to normal dangling bond sites and then annihilate these dangling bonds.

The model mentioned above is considered in more detail using rate equations relevant to the model. In the void region, the as-created dangling bonds (density: \( N_{a1} \)) are photoannealed through nonradiative recombination of electrons and holes at the hydrogen-related dangling bonds, which is expressed by \( B_1 n p N_{a1} \), where \( B_1 \) designates the light-induced annealing coefficient, and \( n \) and \( p \) designate the photoelectron and photohole densities, respectively. In the void region, for simplicity, the hydrogen-related dangling bond density is replaced by the total density of the as-created dangling bonds. Moreover, we assume that \( n \) and \( p \) are expressed by their average values which are proportional to \( G/N \), where \( G \) designates the generation rate of photocarriers and \( N \) is the total density of the as-created and photogenerated dangling bonds (including the dangling bonds in the bulk region), because the photocarrier density is determined by the trapping process at neutral dangling bonds within a time scale faster than the kinetics of light-induced creation and annealing of dangling bonds. The rate equation is given by:

\[
\frac{dN_{a1}}{dt} = -B_1 (G/N)^2 N_{a1}. \tag{1}
\]

In the bulk region, both light-induced creation and annealing of dangling bonds are involved in the rate equation as follows:

\[
\frac{dN_{a2}}{dt} = (A_2 - B_2 N_{a2})(G/N)^2, \tag{2}
\]

where \( N_{a2} \), \( A_2 \) and \( B_2 \) designate the dangling-bond density in the bulk region, the light-induced creation coefficient and the light-induced annealing coefficient, respectively. In the bulk region, for simplicity, we ignore the as-created dangling bonds, thus, \( N_{a2} \) means the density of photogenerated dangling bonds. \( N \) is given by \( N = N_{a1} + N_{a2} \). Eqs. (1) and (2) are transformed into rate equations describing the dangling-bond density relative to the dangling-bond density in the dark. The light-induced creation coefficient, \( a_2 \), and the light-induced annealing coefficient, \( b_2 \), in the bulk region and the light-induced annealing coefficient, \( b_1 \), in the void region defined below determine the rates of respective processes:

\[
a_2 = A_2 G^2/N_1^3, \tag{3}
\]

\[
b_2 = B_2 G^2/N_1^2, \tag{4}
\]

\[
b_1 = B_1 G^2/N_1^2, \tag{5}
\]

where \( a_2 \), \( b_2 \) and \( b_1 \) are in units of \( h^{-1} \) and \( N(t = 0) = N_1 (= N_{a1}(0)) \).

Using the rate equations, we can fit the observed dependence of \( I/I_0 \) and \( I \) on illumination time at RT and 75°C by solid curves in the figures, as shown in Figs. 1 and 2, respectively. The values of parameters, \( a_2 \), \( b_2 \) and \( b_1 \), obtained by fitting of the experimental point, are shown in the figures. Here, we compare the results obtained for He-diluted glow discharge samples used in this study with those obtained for the standard and H₂-diluted glow discharge samples previously studied [1]. The saturated value of \( I/I_0 \) for 0.7 W/cm² illumination in the present sample is greater than that in the previous samples (the standard and H₂-diluted glow discharge samples). From Eqs. (2)–(4), we obtain \( N_{a2}(t = \infty)/a_2 N_1 = b_2 N_1/b_2 \). Then, the saturated value of \( I/I_0 \) is given by \( 1 + (a_2/b_2) \), taking \( b_1 = 0 \). Using this equation, the saturated value of \( I/I_0 \) for 0.7 W/cm² becomes 2.5 times greater than the initial value taken before illumination for the former sample, as shown in Fig. 1; while it becomes 1.1–1.4 times greater than the initial value for the latter samples, depending on preparation conditions [1], where the values of \( a_2 \) and \( b_2 \) range between 0.04 and 0.22 h⁻¹, and 0.25 and 0.58 h⁻¹, respectively [1]. The \( a_2 \) and \( b_2 \) for the present sample are greater than those for the previous samples. These results may be due to difference in hydrogen content and dangling-bond density between the samples. The present samples contain a larger amount of hydrogen and a smaller amount of dangling bonds compared to other types of samples. Note that the dangling-bond density of the present samples is one order of magnitude smaller than that of other types of samples. From Eqs. (3) and (4), \( a_2 \) and \( b_2 \) are inversely proportional to \( N_1^3 \) and \( N_1^2 \).
respectively. Therefore, \(a_1\) and \(b_1\) for sample with a lower dangling-bond density should be greater than those with a higher dangling-bond density. This difference is consistent with the result mentioned above. However, there is a quantitative disagreement. This may be due to differences in \(A_2\) and \(B_2\) between both types of samples.

As shown in Fig. 1, the saturated value of \(I/I_0\) is greater for weak excitation than for strong excitation. This effect shows the importance of light-induced annealing of dangling bonds in the void region as referred to in Ref. [1]. The volume of the sample occupying the bulk region is greater than that occupying the void region, thus, when excitation is weak, electrons and holes are mainly created in the bulk region. Then, the light-induced creation of the dangling bonds in the bulk region becomes dominant. When excitation is stronger, we have some probability for electrons and holes to be photocreated in the void region. This creation leads to process, \(a\), in which the light-induced annealing of dangling bonds plays an important role. This role has already been shown in a-Si:H containing larger amounts of hydrogen and larger numbers of dangling bonds [1]. This phenomenon is associated with the presence of the larger amounts of hydrogen.

Finally, we discuss the results shown in Figs. 2–4. As shown in Fig. 2, the calculated illumination-time dependence of \(I\) using our rate–equation model is not fitted to the experimental points, except for the initial stage of light soaking; but the decay behavior with time is well-fitted by the stretched exponential function as shown in Fig. 3. As shown in Fig. 4, the thermal annealing behavior of dangling bonds created by RT light soaking at 0.7 W/cm\(^2\) is also well-fitted by a stretched exponential function. This fact suggests that the annealing kinetics of dangling bonds in He-diluted glow discharge a-Si:H film is a dispersive process [2–4]. The \(\tau\) and \(\beta\) obtained in Fig. 3 are smaller than those obtained in Fig. 4. These results may be related to the difference between light-induced and thermal annealing processes.

5. Conclusion

The results of light-induced annealing of dangling bonds, as well as their light-induced creation at RT, can be accounted for by using a model previously proposed by us [1], where the model is based on the diffusion and dissociation of hydrogen from hydrogen-related dangling bonds, at which nonradiative recombination of electrons and holes occurs and serves to dissociate nearby hydrogen.

The kinetics of light-induced annealing at 75°C is well-described by a stretched exponential function. The thermal annealing kinetics is also well-described by a stretched exponential function. These facts show that a dispersive process is in effect for the light-induced annealing of dangling bonds at 75°C, as well as for the thermal annealing, in which the dispersive process is associated with hydrogen motion.

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References