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Negatively charged state of atomic hydrogen in *n*-type GaAs

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It is demonstrated that atomic hydrogen drifts as a negatively charged state in *n*-type GaAs and the high electric field strongly affects the dissociation of the hydrogen-donor complex. During reverse-bias-anneal experiments on the Schottky diode, it is confirmed that a negatively charged hydrogen atom is accelerated out of the high-field region and that there is a dissociation-frequency region independent of the anneal temperature. In the dissociation-frequency region dependent on the anneal temperature, the first-order kinetics gives rise to the dissociation energy for the release of the hydrogen–Si donor complex. The dissociation energies are dependent on the applied bias voltage and are in the range of 1.79 to 1.2 eV. Atomic hydrogen in plasma-hydrogenated Si-doped *n*-type GaAs is proposed to be negatively charged with the gain of free electrons and passivates the Si donor, and also the hydrogen or the electron of the hydrogen–Si donor complex to be easily released by the electric field.

Since atomic hydrogen in semiconductors results in electrical passivation of impurity states,[1–6] deep levels[1,7,8] as well as unreconstructed surface dangling bonds,[9] the hydrogen incorporation in crystalline semiconductors has attracted considerable interest.[1–10] Especially the mechanism for the hydrogen passivation and the structures of the hydrogen-defect complexes in GaAs have been investigated experimentally[11–14] and theoretically.[11] Atomic hydrogen diffused into GaAs gives rise to an inactivity of the defects, forming electrically neutral complexes, and is found in a variety of configurations (H^+, H^0, H^-, etc.).[1,15–17] It has been reported that in *n*-type GaAs it may be neutral or negative,[15,16] while in *p*-type GaAs it may be a positively charged state.[5,13] The knowledge of the possible charge states of atomic hydrogen in GaAs is required to understand the complete mechanism of hydrogen passivation and hydrogen-defect incorporation. In spite of this requirement, as compared to that in *n*-type Si,[18,19] the charge state of atomic hydrogen in *n*-type GaAs has been less studied.

The dissociation of hydrogen in the material can be a proof of the charge state and the hydrogen incorporation mechanism. A precise knowledge of the dissociation energy would provide important information in the study of the microscopic configurations of the hydrogen-defect complexes.

In this paper, we report an electric-field-enhanced (EFE) dissociation process of the hydrogen–Si donor (HSD) complex in plasma-hydrogenated *n*-type GaAs. Atomic hydrogen in *n*-type GaAs drifts out of the high-field region as a negatively charged state H^- and the high electric field strongly affects the dissociation of the HSD complex. The precise estimates of the dissociation energy for the release of the HSD complex dependent on the applied electric field are obtained. The passivation and dissociation kinetics of the hydrogen-donor complex is explained by a negatively charged hydrogen.

Si-doped GaAs bulk crystals with a carrier concentration of 1.3×10^{17} cm^{-3} at room temperature were used as starting materials and were exposed to hydrogen plasma at 250 °C in a capacitively coupled rf plasma-enhanced chemical vapor deposition (PECVD) system. The hydrogen pressure during the discharge was 0.57 Torr with a discharge power density of 0.06 W/cm^2. Hydrogenated samples were thermally treated in a vacuum furnace from 200 to 300 °C for a few minutes. The biased anneal was carried out with the fabricated diode from 20 to 180 °C. A Au Schottky diode with a diameter of 0.5 mm was prepared using a thermal evaporator. Before hydrogenation, the samples were chemically etched (H_2SO_4:H_2O_2:H_2O =6:1:1) to a depth of 0.5 μm from the surface in order to eliminate the effects of the mechanically damaged layers. The active carrier concentration and its profile versus junction depth were obtained using a 1-MHz *C-V* measurement controlled by a microcomputer.

The Si donor profiles in hydrogenated and bias-annealed Schottky diode samples were obtained using the *C-V* measurements at room temperature. Figure 1(a) shows the active carrier profiles with the depth in the as-grown sample and the as-hydrogenated sample. In the plasma-hydrogenated sample at 250 °C for 3 h, the carrier concentration decreased by 1 order of magnitude from the surface to 0.25 μm. It is known that the hydrogen passivation by atomic hydrogen is due to form the neutral hydrogen-Si donor complex near the surface region. Figure 1(b) represents the effect of a reverse bias (V_r =5 V) applied during a subsequent vacuum annealing at 150 °C for 160 min. During the 150 °C anneal, the carrier concentration in the diode depletion region (≤ 0.25 μm) is recovered by the high field ($\geq 2\times10^5$ V/cm) applied in

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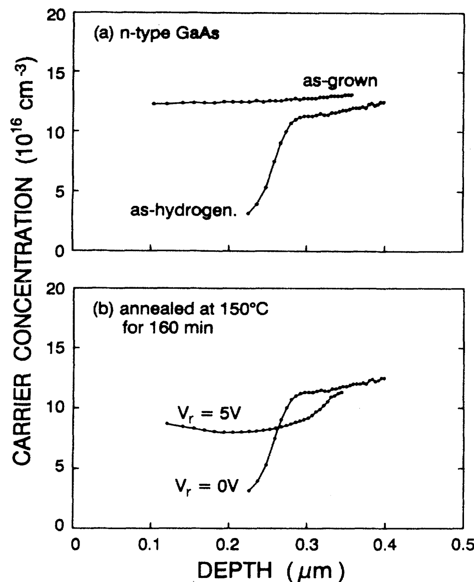


FIG. 1. The carrier concentration profiles according to the depletion depth (a) for as-grown n-type GaAs ($N_d = 1.3 \times 10^{17}$ cm^{-3}) and as-hydrogenated samples at 250 °C for 3 h and (b) for the isothermally annealed sample at 150 °C for 160 min under the -5 V.

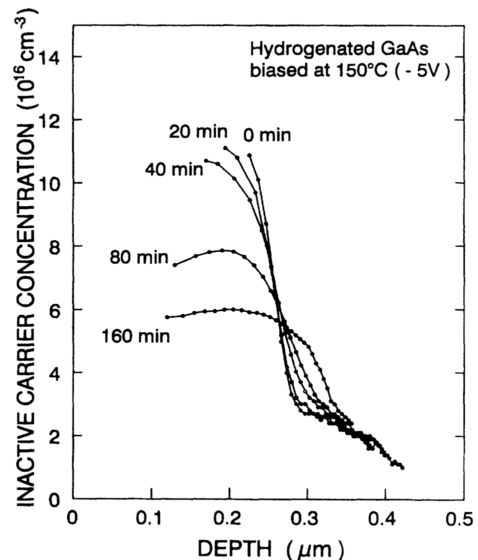


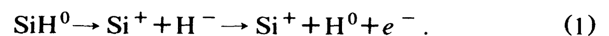
FIG. 2. The inactive donor (N_I) concentration profiles for isothermally annealed samples at 150 °C for various annealing times (t_s) under -5 V. The inactive concentration $N_I(x,t_a)$ is defined as $N_1(x,t_a) = N_{d0}(x,0) - N_d(x,t_a)$. Here, $N_{d0}(x,0)$ and $N_d(x,t_a)$ are active carrier concentrations with depth (x) before and after hydrogenation, respectively.

the region, while the donor passivation occurs in the low-field region up to 0.35 μm.

It is seen that the passivating hydrogen atom is transported into the low-field region of the diode depletion region opposite the Au Schottky contact, and then the neutral carrier in the high-field region is reactivated. However, the passivated carrier is only slightly reactivated in samples annealed at the temperature ranges below 180 °C without the bias for 50 h. This indicates that an applied high electric field apparently affects the rate of dissociation of the neutral HSD complex in n-type GaAs and that atomic hydrogen in n-type GaAs doped with Si drifts as a negatively charge state (H^-).

To investigate the dissociation of the HSD complex in Si-doped hydrogenated GaAs, the depth profile of the inactive donors (N_I) is plotted in Fig. 2 for various annealing times (t_a). The hydrogenated samples were annealed at 150 °C with a reverse bias $V_r = 5$ V and the inactive concentration $N_I(x,t_a)$ is defined as $N_I(x,t_a) = N_{d0}(x,0) - N_d(x,t_a)$. Here, $N_{d0}(x,0)$ and $N_d(x,t_a)$ are active carrier concentrations with depth x before and after hydrogenation, respectively. Considering the inactive Si donor as the HSD complex, the HSD concentration in the as-hydrogenated sample ($t_a = 0$) is about 1.1×10^{17} cm^{-3} in the passivation region ($x \leq 0.25$ μm), while above the region ($x \geq 0.25$ μm) it decreases rapidly. As the increase of the annealing time, the HSD concentration in the depletion region ($x \geq 0.25$ μm) decreases gradually, reaching to 6×10^{16} cm^{-3} after 160 min anneal. On the other hand, the HSD concentration above the region ($x \geq 0.25$ μm) increases and the HSD complex drifts toward deeper region during biased annealing. The drift of the HSD complex can be explained as the migration of the charged monatomic hydrogen. As the charged atomic hydrogen is removed from the high-field regions of the depletion layer towards the low-field region, the Si donor in the high-field region is reactivated to its original quantity while the active donor in the low-field region is passivated. From the fact that the HSD complex does not drift during annealing at 150 °C without the reverse bias but drifts markedly away from the surface with a reverse bias, it is confirmed that the applied high electric field apparently affects the rate of dissociation of the HSD complex and the atomic hydrogen in n-type GaAs doped with Si is negatively charged.

By using above results, the formation and dissociation of the HSD complex in n-type GaAs doped with a Si donor can be explained as a mechanism similar to recent reports.[1,6,20,21] The atomic hydrogen diffused into n-type GaAs by the rf plasma exits as a negatively charged species with the gain of the an electron and then the negatively charged hydrogen atom, H^-, is bound to a Si donor according to the relation $Si^+ + H^0 + e^- \rightarrow SiH^0$. The reaction passivates the active Si donor and forms the neutral HSD complex, SiH^0. Since the HSD complex is loosely bound to the nearest atom because of the charged hydrogen atom and then the hydrogen atom with an electron can easily released by the electric field, the electrically driven or the thermally activated dissociation can also occur with the loss of the electron and/or the hydrogen atom. This is, the HSD complex is dissociated according to the relation



$$SiH^0 \rightarrow Si^+ + H^- \rightarrow Si^+ + H^0 + e^- . \quad (1)$$

During the drift of H^- which is dissociated in the high-field region, it is possible that a recombination reaction $Si^+ + H^- \rightarrow SiH^0$ occurs in the low-field region and that some H^- is lost in the high-field region due to charge-

state conversion into H^0 or H^+ that interrupts the electric-field enhanced drift of hydrogen atom.

Using the first-order kinetics[3] for the inactive carrier concentrations in Fig. 2, we investigate the dissociation kinetics.

$$N_I(x,t_a) = N_{I0}\exp[-\nu_d(T_a)t_a] \quad (2)$$

with

$$\nu_d(T_a) = \nu_{d0}\exp(-E_d/kT)\,, \quad (3)$$

where T_a and t_a are the annealing temperature and time, respectively. E_d is the dissociation energy, and ν_d the dissociation frequency. N_{I0} is the maximum inactive carrier concentration, i.e., a difference of the carrier after and before passivation. The first-order reactivation of the carrier was considered for the samples isochronally annealed with the reverse bias voltage at the temperature range below 180 °C. And, without the reverse bias the samples were annealed in the ranges of 220–300 °C.

Figure 3(a) represents the data corresponding to various temperatures 220, 240, 260, and 300 °C. The calculated dissociation frequencies ν_d(220–300 °C) are in the range of $(1.15\text{–}38.4)\times10^{-4}$ s^{-1}. And they follow the Arrhenius equation $\nu_d(T_a) = 5.7\times10^{13}\exp(-1.79\pm0.05$ $eV/kT_a)s^{-1}$. The dissociation energy 1.79 ± 0.05 eV determined in Si-doped GaAs with a carrier concentration of 1.3×10^{17} cm^{-3} corresponds to the energy required to fully release hydrogen atom from the Si donor. It is believed that the small dissociation energy in comparison with a reported value[3,4,22,23] can be due to the effect that during the diode annealing in vacuum the removal of the HSD complex is accelerated in the space-charge region near the surface. Figure 3(b) shows the dissociation process of the inactive carrier that was obtained after isothermal anneals with a bias voltage. The hydrogenated samples were thermally annealed under the reverse bias 5 V at various temperature in the range of 130–190 °C. During first 20-min annealing, the dissociation process has only one frequency 1.02×10^{-4} s^{-1} for various annealing temperatures, while for a further 50 min it shows different values for each temperature. Here, the starting point (20 min) for different dissociation frequency defines two frequency regions, (I) and (II). As the annealing time increases, the donor is progressively reactivated in region (I) independent of annealing temperatures, while the reactivation becomes less pronounced in region (II). Considering that the dissociation frequency in region (I) during the 10-V-biased anneal[21] was 1.49×10^{-4} s^{-1}, which is slightly higher than the value in the 5-V-biased sample, it is suggested that the high electric field in the depletion region directly takes part in initial dissociation process (I). In region (II) during isothermal anneals with the 5-V reverse bias, the dissociation of the HSD complex also follows first-order kinetics.

Arrhenius plot of the dissociation frequencies in region (II) is shown in Fig. 4. The plot for the 5-V-biased anneal yields a dissociation energy E_d of 1.47 ± 0.05 eV and a dissociation frequency ν_{d0} of 2.8×10^{13} s^{-1}. Table I shows our results in the biased-anneal samples compared to the data reported in the literature. In Refs. 3 and 4, the isothermal anneal was performed on no device and unbiased hydrogenated samples. Also, in our biased-anneal results, a first-order kinetics to obtain E_d is assumed in dissociation region (II). Dissociation energies in biased-anneal samples are low with the increase of the applied voltage. Among these plots, the first-order fit ($E_d = 1.2\pm0.1$) in the 10-V-annealed samples is poor in the space-charge region. It is difficult to obtain exactly the required electric field on the metal-semiconductor structure

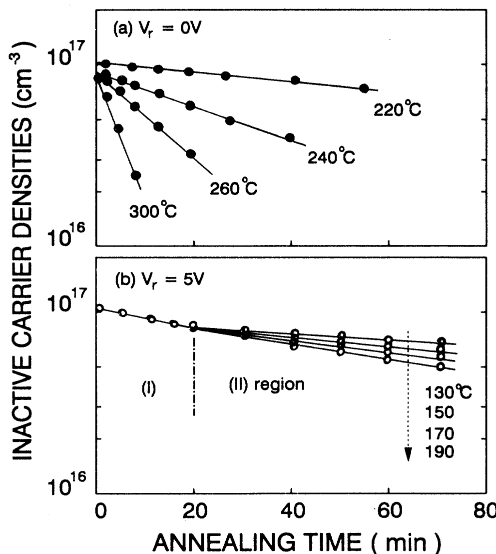


FIG. 3. The inactive carrier concentrations $N_I(x,t_a)$ with annealing times t_a (a) for no-biased anneals at 220, 240, 260, and 300 °C, and (b) for 5-V-biased anneals at 130, 150, 170, 190°C, respectively. In this figure, the starting time (20 min) for different dissociation frequency defines two frequency regions, (I) and (II).

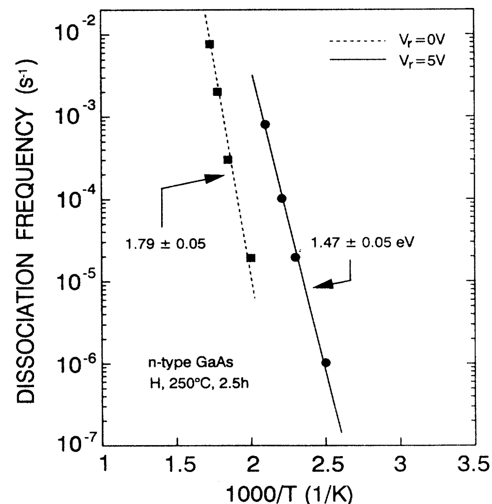


FIG. 4. Arrhenius plot of the dissociation frequencies in the (II) region in Fig. 3. In the 5-V-biased annealed sample, the first-order kinetics yields a relation $\nu_d = 2.8\times10^{13}$ exp $(-1.47\pm0.05$ $eV/kT_a)s^{-1}$, while in the unbiased annealed sample $\nu_d(T_a) = 5.7\times10^{13}\exp(-1.79\pm0.05\ eV/kT_a)s^{-1}$.

TABLE I. Dissociation frequencies and energies according to the electric field.

	ν_{d0} (10^{13} s^{-1})	E_a (eV)	N_d (10^{17} cm^{-3})
No device[a]	10	2.1 ± 0.05	10
0 V	5.7	1.79 ± 0.05	1.3
−5 V	2.8	1.47 ± 0.05	1.3
−10 V	13	1.2 ± 0.1	1.3

[a]Data from Refs. 3 and 4.

because a space-charge width generally increases with the increase of the reverse bias and depends on the distribution of charge traps or impurities. Therefore, high-field experimental values are thought to be able to scatter according to the applied field. Zundel and Weber[24] reported that for shallow acceptor in Si the dissociation frequencies ν_d were independent of the applied reverse bias voltage. But, from the fact that the EFE dissociation in *n*-type GaAs occurs even at room temperature,[21] it is assumed that the applied electric field strongly affects the dissociation frequency and energy of the neutral HSD complex in *n*-type GaAs.

In conclusion, we have presented the drift of atomic hydrogen as a negatively charged state in *n*-type GaAs. In the dissociation frequency region dependent on the biased-anneal temperature, using the first-order kinetics, it is obtained that the precise estimates of the dissociation energy for the release of the hydrogen–Si donor complex are dependent on the applied electric field and are in the range 1.79–1.2 eV. These results provide that the high electric field can strongly affect the dissociation of the HSD complex in GaAs and accelerate a negatively charged H^- out of the space-charge region.

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