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Light-enhanced reactivation of donors in hydrogenated *n*-type GaAs

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The donors in undoped and S-doped GaAs are passivated by exposure to a hydrogen plasma. The influence of laser illumination (1.54 eV) on the reactivation of the passivated donors at 100 °C is investigated. It is found that the dissociation of the donor-hydrogen complex is greatly enhanced under illumination. The reactivation of the passivated donors follows an initially fast process, which for long annealing times reduces to a reactivation process obeying second-order kinetics. The rate-limiting process is explained in terms of the combination of two hydrogen atoms into a molecular species.

There is considerable current interest in the hydrogenation of GaAs, due to the ability of hydrogen to passivate the electrically active impurities and defects present in the material. In both *n*- and *p*-type GaAs, passivation of the shallow impurities results from the formation of electrically neutral dopant-hydrogen complexes.[1-3] Before the possible benefits of hydrogenation can be applied to processing techniques and technological applications, however, the important question regarding the thermal stability of the dopant-hydrogen complex under normal operating conditions needs to be addressed.[3] In spite of many investigations of the properties of H in GaAs, relatively little is known about either the stability of the complexes, or the kinetics governing their dissociation. The major studies in this regard have been conducted by Pearton *et al.*[4] By using capacitance-voltage (*C*-*V*) measurements to obtain the carrier density profiles in a series of hydrogenated *n*-type GaAs samples, that had been isochronally annealed in the temperature range 250–400 °C, they measured a dissociation energy of about 2.1 eV for the donor-hydrogen complexes, *D*H (*D* = Si, Se, S, Te, Sn and Ge). In their calculations, they implicitly assumed that the reactivation process obeyed first-order kinetics. By contrast, in a recent study[5] of H-passivated Se-doped GaAs, we found that the thermal reactivation process obeyed first-order kinetics throughout the entire annealing time, *provided* the thermally dissociated hydrogen was drifted away from Se (through the application of an electric field) to prevent the SeH complex from again forming when cooling the sample. From our *C*-*V* measurements we determined a smaller dissociation energy of 1.52 eV for the SeH complex.[5]

There is only minor reported evidence for the influence of light on the passivation of GaAs. For *p*-type GaAs, Szafranek *et al.*[6,7] reported a light-induced reactivation (LIR) effect occuring at low temperatures during photoluminescence measurements on *p*-type GaAs. They attributed this reactivation process to electron-hole pair trapping at the acceptor-hydrogen complexes.[7] Tavendale *et al.*[8] reported that acceptor passivation in *p*-type GaAs is unstable to minority-carrier injection by illumination at 25 °C. They showed that the reactivation of the acceptors under illumination did not result from direct photodissociation of the acceptor-hydrogen complex, but could be attributed to minority-carrier injection. No investigation of the kinetics controlling the dissociation process was, however, reported. For the case of *n*-type GaAs, there is also a clear need for the effects of light on the stability of the donor-hydrogen complex to be investigated.

In this paper we show that the thermal dissociation of the donor-hydrogen complex in *n*-type GaAs is greatly enhanced under illumination. Furthermore, it is found that the reactivation process may be described by second-order kinetics. The rate-limiting process is the recombination of two hydrogen atoms into a molecular species.

The GaAs material used in this work consisted of 5-μm thick S-doped GaAs ($n = 7 \times 10^{16}$ cm^{-3}), grown by metalorganic vapor phase epitaxy (MOVPE) on an undoped semi-insulating GaAs substrate. Some measurements were also performed on 10-μm thick undoped ($n = 2 \times 10^{15}$ cm^{-3}) GaAs layers, also grown by MOVPE. AuGe-Ni Ohmic contacts were formed on corner sections of the epitaxial layer surfaces. Hydrogen was then introduced into the material at 180 °C by exposing it for 2 h to a hydrogen plasma in a remote dc plasma system.[9] During hydrogenation the samples were mounted on a heater block about 10 cm downstream from the plasma (i.e., outside the direct plasma). Further details of the hydrogenation process have been given previously.[5]

After passivation, the GaAs was lightly etched for 40 s in H_2SO_4:H_20_2:H_20 (1:8:160) to remove approximately 0.2 μm off the plasma-exposed surfaces. This was to prevent the possibility of surface-related defect states (originating from the plasma treatment) influencing the electrical measurements to be performed. Semi-transparent (~ 30 nm thickness) Au Schottky contacts (1 mm diameter) were then evaporated on the etched surfaces. In order to determine the depth of the passivation in the GaAs, some Schottky contacts were evaporated directly on the as-passivated (nonetched) surfaces. Schottky diodes were also fabricated on a reference sample that had not been exposed to the plasma.

Capacitance-voltage (C-V) measurements at 1 MHz were used to profile the net donor concentration in a S-doped GaAs layer at room temperature. The measured concentration after hydrogenation was 1×10^{16} cm^{-3}, with the passivation extending to a depth of about 0.5 μm. Identical carrier concentration profiles were obtained from C-V measurements at 77 K. We therefore rule out the possibility of compensating deep levels causing the measured reduction in carrier concentration after hydrogenation. Rather, this reduction from a bulk value of 7×10^{16} cm^{-3} is attributed to the formation of the electrically neutral SH complex. Thus S-doped GaAs can be efficiently passivated, using the above-mentioned hydrogen plasma conditions.

The influence of light on the thermal dissociation of the SH complex was investigated, by focusing the emission from an Al$_x$Ga$_{1-x}$As power laser diode ($\lambda = 802$ nm, $E = 1.54$ eV) onto a semitransparent Schottky contact, while annealing at 100 °C. In order to minimize edge effects, the diameter of the laser spot was set larger than the Schottky contact. After an annealing time t, the temperature was rapidly decreased to room temperature by briefly immersing the sample holder in liquid nitrogen. The Schottky diode, which was kept in the open-circuit configuration during the annealing cycle, remained in the dark for both the heating and cooling steps. The incident photon flux was monitored by measuring the photocurrent I_{ph} of the Schottky diode under reverse bias conditions at room temperature, before and after each anneal. By measuring the photon flux ϕ with a power meter, we have found that for the photocurrent range used in this study ($10-100$ μA), $\phi = \gamma I_{\text{ph}}$, with $\gamma = 189$ mW cm^{-2} mA^{-1}. It has been shown[10] that for even larger power densities, the possibility of localized heating of the sample during illumination is negligible.

Figure 1 shows a series of carrier concentration profiles measured on the same Schottky diode, after annealing under laser illumination ($I_{\text{ph}} = 100$ μA) at 100 °C. For increasing annealing times t, there is a progressive reactivation of the S donors, with a corresponding increase in the carrier concentration. After 27 h, the majority of the S donors have been reactivated, leading to a restoration of the original carrier concentration of the GaAs. By comparison, annealing another hydrogenated S-doped sample in the dark for a similar time yielded no noticeable change in the carrier concentration profile. Thus the reactivation of the passivated S donors may be directly attributed to the influence of the incident light during the annealing cycle. Furthermore, the rate of reactivation was found to be very sensitive to the photon flux incident on the Schottky contact.

The carrier concentration profiles of Fig. 1 represent the electrically active S-donor concentration, $N(t)$, in the GaAs. In order to quantitatively analyze the reactivation of the SH complexes, we have measured the inactive donor concentration $R(t) = N_0 - N(t)$ at $x = 0.2$ μm. To obtain an accurate value of the original S-donor concentration N_0, the annealing process was continued until no further reactivation could be detected. The plot of $\ln R(t)$ versus t is found to strongly deviate from a linear relationship, indicating that the reactivation of the S donors does *not* follow first-order kinetics. By contrast, Fig. 2 shows that a linear relationship is obtained from the plot of $R^{-1}(t)$ vs t. With the exception of data for short annealing times, where there is a deviation from linearity, the straight line seen in Fig. 2 implies that the reactivation process can be described by the second-order equation:

$$\frac{dR}{dt} = -r'R^2, \tag{1}$$

where the second-order annealing parameter $r' = 4 \times 10^{-21}$ cm^3/s at $x = 0.2$ μm. Deeper into the GaAs ($x = 0.25$ μm), the value obtained for r' is slightly higher (6×10^{-21} cm^3/s).

In a similar manner we have examined the reactivation of the donors in nominally undoped ($n = 2 \times 10^{15}$ cm^{-3}) GaAs, by annealing at 100 °C with light ($I_{\text{ph}} = 10$

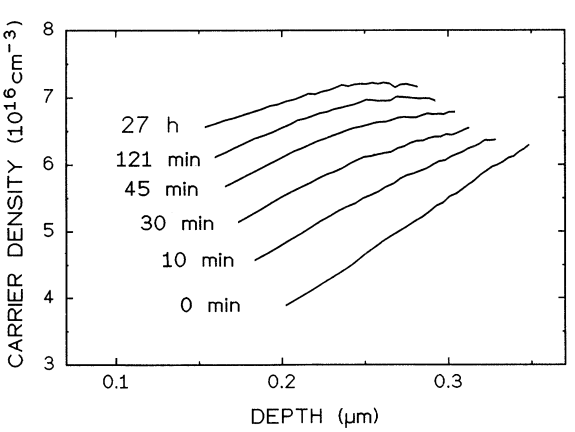

FIG. 1. Carrier concentration profiles in hydrogenated S-doped GaAs, after annealing at 100 °C with light ($I_{\text{ph}} = 100$ μA) for increasing annealing times t.

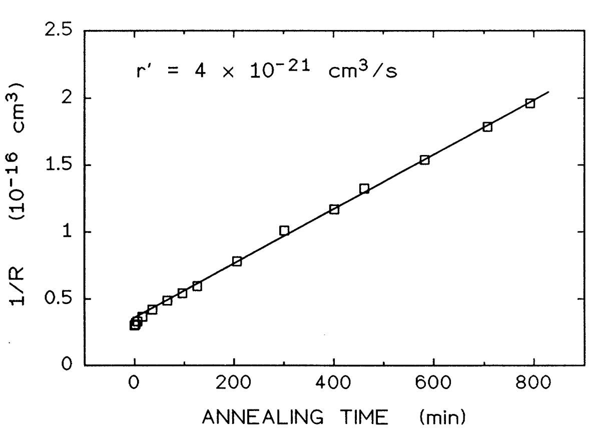

FIG. 2. Analysis of the annealing kinetics describing the reactivation process of Fig. 1. The inactive donor concentration R was measured at a depth $x = 0.2$ μm. The solid line represents the fit of the data to Eq. (1), for $t > 60$ min.

μA). We again obtain a second-order reactivation process, qualitatively similar to the results of Fig. 2. The annealing parameter $r' = 4 \times 10^{-19}$ cm$^3/s$ is, however, two orders of magnitude larger than what was measured in S doped GaAs, in spite of the much smaller laser photocurrent used for the undoped GaAs. We conclude that the rate of reactivation of the donors is strongly dependent on the concentration of donor-hydrogen complexes in the material. As before, no change in the carrier concentration is measured when annealing at 100 °C in the dark.

We interpret the reactivation process of Fig. 1 in the following manner: The dissociation and formation of the electrically neutral SH complexes is described by the following reaction and kinetic equation:

$$(\mathrm{SH})^o \rightleftharpoons \mathrm{S}^+ + \mathrm{H}^- \tag{2}$$

$$\frac{\partial[\mathrm{SH}]}{\partial t} = \sigma[\mathrm{H}](N_0 - [\mathrm{SH}]) - \nu_{\mathrm{SH}}[\mathrm{SH}], \tag{3}$$

where [H] and [SH] are the concentrations of free atomic hydrogen and SH complexes, respectively, N_0 is the uniform S donor concentration in the nonhydrogenated sample, σ is the capture coefficient of the atomic hydrogen by the active S donors, and ν_{SH} is the dissociation frequency of the SH complex. The first term on the right-hand side of Eq. (3) describes the formation of SH complexes, while the term ν_{SH}[SH] describes their dissociation.

The reactivation of the S donors implies that reaction (2) must proceed predominantly to the right. The dissociated H, which will be in a negatively charged state immediately upon dissociation,[5] must therefore either be removed from the vicinity of the ionized donor, or converted into an electrically inactive state. We have previously found[5] that the thermally dissociated H can be drifted away from the ionized donors by the electric field within the space-charge region of a reverse-biased Schottky diode, when annealing at 150 °C. This results in the local concentration of H remaining negligible and Eq. (3) reducing to a first-order equation, which is experimentally measured.[5] In the present case, however, the absence of an electric field rules out the possibility of H drift from taking place. Furthermore, the carrier concentration profiles of Fig. 1 do not support the possibility of an out diffusion of H during the annealing process.

We therefore conclude that the H, upon dissociation from the ionized donor, is converted into a state that is both electrically inactive and stable, for temperatures up to at least the annealing temperature (100 °C). The fact that the reactivation process can clearly be described by second-order kinetics, as seen in Fig. 2, suggests that the negatively charged hydrogen (H^-) is converted into some molecular form, according to the following reactions:

$$\mathrm{H}^- \longrightarrow \mathrm{H} + e^- \tag{4}$$

and

$$\mathrm{H} + \mathrm{H} \longrightarrow \mathrm{H}_2. \tag{5}$$

The energy of the incident laser beam (1.54 eV) is greater than the band gap of the GaAs [1.39 eV at 100 °C (Ref. 11)]. During the annealing process, the incident light will therefore be absorbed within a depth determined by the absorption coefficient. This corresponds to a depth of approximately 1 μm,[12] where electron-hole pairs will be generated. The injected minority carriers (holes) will diffuse to the vicinity of the dissociated hydrogen, thereby enhancing the conversion of H^- into H, according to reaction (4). This explains why the rate of reactivation of the S donors was found to be so sensitive to the incident photon flux. On the other hand, when annealing at 100 °C in the dark, the absence of generated minority carriers removes the driving force for reaction (4) to occur and no reactivation is measured.

Returning to Fig. 2, it is noted that the initial reactivation of the S donors occurs at a faster rate than that described by second-order kinetics. Even for this initial reactivation, however, it was not possible to use first-order kinetics to describe the process. For more clarity, we have replotted the relevant section of Fig. 2 on an expanded time-scale in Fig. 3 (left-hand axis). Such an effect has been reported before for the reactivation of hydrogenated B-doped Si.[10] In that case, the enhanced reactivation was found to satisfy the following equation:

$$\frac{dR}{dt} = -r\frac{R^2}{(N_o - R)^2}, \tag{6}$$

where the annealing parameter r is related to r' by $r = r'/N_D^2$. Equation (6) was derived[10] by assuming that reaction (2) occurs faster than reaction (4). Dynamic equilibrium is then achieved for reaction (2) ($d[\mathrm{SH}]/dt = 0$). For short annealing times, the assumption that most of the hydrogen remains trapped at the S donors ([H]≪[SH]) leads to Eq. (6). The integral form of Eq. (6) is

$$S(t) = rt + S_{t=0} \tag{7}$$

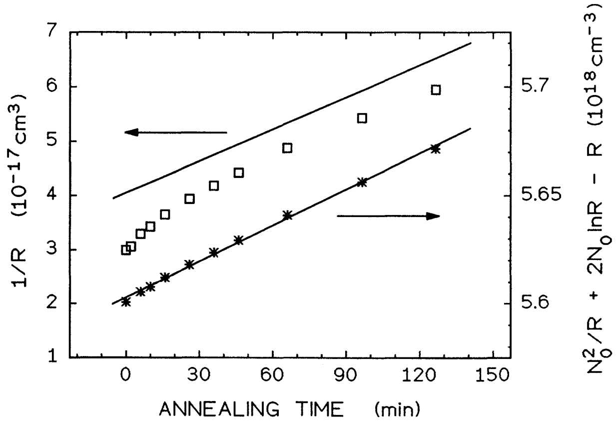

FIG. 3. Analysis of the annealing kinetics based on Eq. (1) (□, left-hand scale) and Eq. (6) (+, right-hand scale), for short annealing times ($t < 120$ min). The solid lines represent the fit of the data to Eq. (1) (for $t > 60$ min) and Eq. (6), with $r' = 4 \times 10^{-21}$ cm^3/s and $r = 9 \times 10^{12}$ cm^{-3}/s, respectively.

with $S = N_o^2/R + 2N_o \ln R - R$. In Fig. 3 (right-hand axis) we have plotted $S(t)$ vs t, from which we obtain a linear dependency with an annealing parameter $r = 9 \times 10^{12}$ cm^{-3}/s. It is seen that Eq. (6) satisfactorily describes the initial fast reactivation process of Fig. 2. For $R \ll N_o$ (long annealing times), however, Eq. (6) reduces to the standard second-order form given by Eq. (1).

To conclude, we have shown that the passivated donors in hydrogenated undoped and S-doped *n*-type GaAs may be reactivated at 100 °C by annealing under illumination. The reactivation follows an initially fast process, which for long annealing times reduces to a second-order kinetic equation. The rate-limiting process is found to be the combination of two hydrogen atoms in a molecular species. Although from our measurements we cannot derive further information regarding the structure of the molecular species, it is electrically neutral and stable up to at least the annealing temperature. One possibility is that the hydrogen becomes trapped at lattice vacancy clusters, forming hydrogen platelets, which have been reported by Neethling and Snyman.[13] Finally, our results show that the donor-hydrogen complex in passivated *n*-type GaAs is very unstable to light. This may have important implications when applying the H passivation treatment to both optoelectronic and other devices.

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