Reactivation kinetics of acceptors in hydrogenated InP during unbiased annealing

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(Received 22 July 1994)

The reactivation kinetics of passivated Mg acceptors in hydrogenated InP during unbiased annealing of a Schottky diode is reported. The reactivation is found to slow down gradually with annealing time and this phenomenon is attributed to substantial retrapping of H at the acceptor sites. It is found from the concentration profiles and the kinetics data that the reactivation is most likely limited by H_2 molecule formation processes for longer annealing times; for shorter annealing times, contributions from indiffusion of H also become significant. The diffusion of H during the initial period follows an Arrhenius relation with an activation energy for the effective diffusion coefficient of 1.13 ± 0.10 eV. In the H_2 formation regime, the reactivation is thermally activated with an activation energy for the annealing parameter of 1.71 ± 0.10 eV. The H_2 formation-limited regime of reactivation occurs sooner as the annealing temperature is increased.

I. INTRODUCTION

The introduction of atomic hydrogen leads to electrical deactivation of shallow dopants, deep levels, and other defects in virtually all the semiconductors.[1-10] The dopant passivation is generally attributed to the formation of a neutral dopant-hydrogen complex.[1] As H gets incorporated inadvertently in the semiconductor during a variety of processes,[1] it is important to understand the stability of passivation under different conditions. This information is also essential for the fabrication of devices based on hydrogenation.[11-14] The passivation effects can be removed by a suitable thermal anneal[1,2] and/or by a minority carrier injection.[15] In order to study the thermal stability of passivation, quantities such as the complex dissociation frequency and the dissociation energy assume importance. Zundel and Weber[4] used a reverse-bias annealing (RBA) technique to estimate these quantities accurately. In this technique, the applied reverse bias during annealing sweeps the thermally liberated charged hydrogen away from the high-field region, thereby reducing the possibility of retrapping at the acceptor sites in the same region. The retrapping, if allowed to occur, would effectively reduce the dissociation and hence an accurate estimate of the actual dissociation parameters is not possible.

The thermal reactivation of dopants in the presence of a reverse bias has been studied for n- and p-type Si,[3,4] n- and p-type GaAs,[5-7] and p-type InP.[8,9] In all these cases, the reactivation follows a simple first-order kinetics and the analysis is quite straightforward. In contrast, the reactivation in the absence of a reverse bias presents a more complex picture. While the RBA technique gives more accurate estimates for the dissociation parameters,

the case of annealing without bias is also important as it presents a situation close to the material processing conditions. Therefore, a detailed analysis of the reactivation mechanism during zero-bias annealing (ZBA) is required.

The dopant reactivation mechanisms during ZBA have been reported by various authors for Si (Refs. 15 and 16) and n-GaAs.[6] Zundel and Weber[15] (ZW) proposed a new kinetic model to explain the boron reactivation process in hydrogenated Si during unbiased annealing. Their data showed that the annealing process is rate limited by the formation of a stable electrically inactive complex involving two H atoms. Cho et al.[6] fitted their data to a simple first-order equation and obtained a high dissociation energy which they attributed to the low electric field during ZBA. In this paper, we examine the processes involved in the reactivation of Mg acceptors in hydrogenated InP during unbiased annealing of Au/p-InP Schottky diodes. It is found that the model of ZW holds good only for the longer-time annealing. In the shorter-time regime, the contribution of in-diffusion of H also becomes important in explaining the reactivation process.

II. EXPERIMENTAL DETAILS

The InP used in this work were commercially procured liquid encapsulated Czochralski grown crystals which are Mg doped to a concentration of 5.8×10^{16} cm^{-3}. The samples were degreased, etched in H_2SO_4:H_2O_2:H_2O (1:1:8) solution, treated in dilute HF for native oxide removal, rinsed in running de-ionized water, and blown dry with nitrogen. A full area back ohmic contact to the wafers was formed by depositing Au/Au-Zn (50/1000 Å) layers and alloying at 430 °C for 30 s in an inert atmosphere. During this step the wafers were kept face down

on another InP wafer. The wafers were then subjected to a radio frequency (13.56 MHz) hydrogen plasma exposure. The method of hydrogenation has been discussed in earlier publications.[17,18] The plasma treatment was carried out for 60 min with an rf power of 0.5 W/cm^2, sample temperature maintained at 200±2 °C and the chamber pressure controlled at 0.5 torr. After the treatment, Au Schottky dots of 0.6-mm diameter were deposited through a shadow metal mask.

The barrier height of the diodes was about 0.8 eV as measured from the I-V characteristics. The active acceptor concentration profile was evaluated from 1-MHz C-V measurements carried out at room temperature using a Boonton capacitance meter controlled by a computer. Where possible, small forward bias was also used for C-V measurements in order to probe depths closer to the surface. The thermal annealing was performed in the temperature range 200–245 °C for different times ranging from several minutes to several hours with the diode terminals shorted. The temperature was controlled within ±1 °C. After annealing, the diode was rapidly cooled down to room temperature by dipping the sample holder in liquid nitrogen. The acceptor profile was extracted after every such anneal. The time taken for the sample to reach the annealing temperature was typically 30 s which was considerably smaller compared to the duration of annealing. The Au Schottky contacts were stable against these annealing treatments as evidenced from the nearly unaffected I-V characteristics of the diodes.

III. RESULTS AND DISCUSSION

Figure 1 shows the C-V depth profiles of the active acceptor concentration (N_{act}) in the InP samples after a 245 °C anneal for different durations. The uniform concentration (N) of the acceptors in the unhydrogenated control sample is also shown. It can be observed that hydrogenation results in the passivation of the acceptors, reducing its effective concentration to below 10^{15} cm^{-3} up to a depth of nearly 1.8 μm. The passivation is generally understood as being due to the formation of neutral

acceptor-H complexes. The annealing debonds the complexes and reactivates the acceptors. The bonding and debonding of H with the acceptor can be explained by the reaction[1,2]

$$[AH] \rightleftharpoons [A^-] + [H^+] , \qquad (1)$$

where $[AH]$, $[A^-]$, and $[H^+]$ are the concentration of acceptor-H complex, acceptor, and free hydrogen, respectively. Our earlier RBA experiments have shown the positively charged nature of H in p-InP.[9] To understand the reactivation process, the inactive acceptor concentration given by $N_{In} = N - N_{act}$ measured at a depth of 1 μm is plotted as a function of time for different annealing temperatures, as shown in Fig. 2. It can be seen that N_{In} reduces with an increase in time and the process is nonexponential. This kind of reactivation is different from what one normally observes for annealing with a reverse bias wherein the reactivation is faster following an exponential first-order process.[4] Apparently, a slow reactivation in the case of annealing without bias is due to a substantial retrapping which reduces the effective dissociation of the acceptor-H complexes.

During annealing, the acceptor reactivation occurs as a result of two processes, namely, thermal dissociation of the complex and removal of the liberated H away from the acceptor in order to minimize retrapping The removal can be brought about by processes such as (i) electric-field-induced drift when the H is in a charged state, (ii) H diffusion into the bulk, and (iii) H_2 formation, which renders H electrically inactive. Of these, the electric-field-induced drift is the most efficient and in fact forms the basis of the RBA technique[4] to estimate the dissociation frequency and energy accurately. In the absence of a reverse bias, the other two processes can dominate the reactivation kinetics. The role of these processes in the reactivation is explained in the following.

(a) The concentration gradient of the active acceptors and associated electric field would lead to H migration into the bulk. As time progresses, the migration would become less effective due to the reduced gradient and
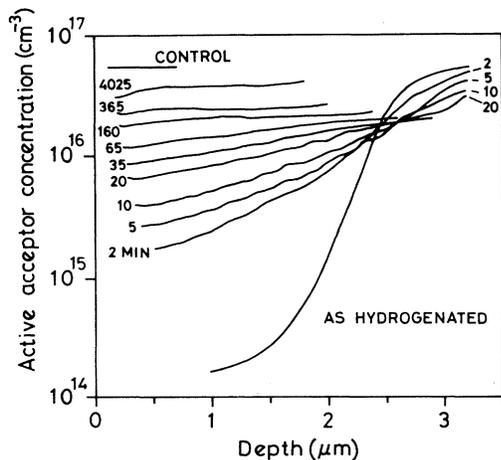

FIG. 1. Net active acceptor concentration profiles after annealing at 245 °C for different times.

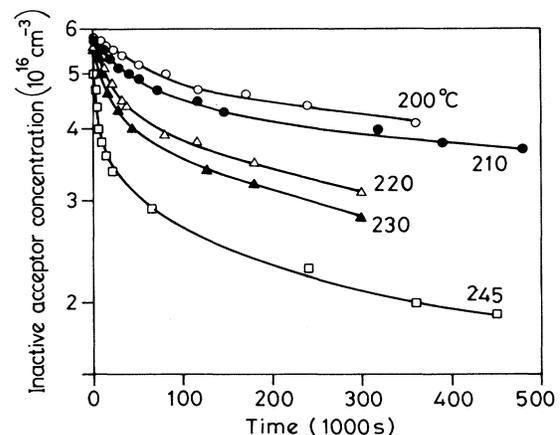

FIG. 2. Inactive acceptor concentration at a depth of 1 μm after annealing at different temperatures as a function of annealing time.

hence reduced field. The less effective migration would lead to increased retrapping and hence the reactivation can get slower with time.

(b) H_2 molecule formation would occur when two liberated H atoms combine with each other. This rate is much slower compared to that of H retrapping at the acceptor sites. This is because H_2 formation takes place by the complexing of H^0 and H^+, H^+ and H^+, or H^0 and H^0 whereas the retrapping of H at the acceptor site is guided by Coulombic attraction as H is predominantly present as H^+ in p-type materials.[4,7-9] Therefore, when the reactivation is limited by molecule formation, the large retrapping effectively slows down the process.

Sah, Pan, and Hsu[19] fitted their annealing data on acceptor-H complexes in Si metal-oxide-semiconductor structures to a first-order kinetic model for short annealing times and to a second-order equation for longer times. In their analysis, the initial first order was explained by assuming a nearly constant H concentration with time during which dynamical equilibrium is not attained for the reaction (1). The long-time second-order process was explained by the H_2 molecule formation. Zundel and Weber[15] developed a kinetic model that explains the reactivation of boron in hydrogenated Si for all the measured annealing times in the temperature range 100–200 °C. Their experiments feature negligible long-range H indiffusion. They showed that dynamical equilibrium is always achieved for the reaction (1) and in the absence of H diffusion, the formation of H_2 molecule is the rate limiting step even for shorter annealing times.

We find that the present set of data does not follow first-order kinetics even for shorter times. Therefore, in order to identify the mechanisms involved in the reactivation process in the present case, we first fit the data to the model of ZW.[15] According to this model, the reactivation is described by the relation,

$$S(t) = rt + S(0),$$ (2)

where

$$S(t) = \frac{N^2}{N_{In}} + 2N\ln N_{In} - N_{In}.$$ (3)

r is the annealing parameter and t is the annealing time. The derivation of (2) and (3) is based on the formalism that H_2 molecule formation is the only mechanism for H removal to reactivate the acceptors and that $[AH]$ is nearly invariant in time. The latter condition corresponds to the attainment of dynamical equilibrium for reaction (1). An independent estimate of the time scales in the present case indicates that dynamical equilibrium is achieved at times much shorter than the experimental annealing times for all the temperatures studied. This estimate was made using the Arrhenius relation for the acceptor-H complex dissociation frequency (v_d) obtained from our earlier RBA experiments on Mg-doped InP samples.[9] During RBA, the complex dissociation takes place at a rate determined by an activation energy of 1.40 ± 0.08 eV and a prefactor of $1.3–3.1 \times 10^{13}$ s^{-1}. The inverse of the dissociation frequency provides the upper

limit for the equilibration time since the v_d from RBA experiments corresponds only to the forward reaction in Eq. (1). In the presence of retrapping, the backward reaction would further reduce this equilibration time. The plots of the function $S(t)$ for two annealing temperatures are shown in Fig. 3. Evidently, the fits are good for longer annealing times whose slope gives the value of r, the frequency with which the reactivation of acceptors in a unit volume takes place through the process of H_2 formation. For shorter times, the data deviates from the model. This deviation points to lower values of r for shorter times and this means that the contribution of H_2 formation to the reactivation is minimal. This is unlike the data of ZW[15] which fit to the model even for short annealing times. The transition from a *shorter* to a *longer* annealing time regime in our data occurs sooner as the temperature is increased. The annealing parameter r follows the Arrhenius relation

$$r = 3.1 \times 10^{27}\exp\left[\frac{-(1.71 \pm 0.10) \text{ eV}}{kT}\right]$$ (4)

as shown in Fig. 4. The activation energy given in Eq. (4) is the sum of the activation energy for H migration, the capture energy barrier for H_2 formation, and twice the binding energy of the acceptor-H complex. As yet, little is known about these energy values individually for H in InP.

The deviation of the shorter-time reactivation process away from the molecule formation model warrants additional considerations. As can be seen from Fig. 1, annealing for shorter times results in profiles that are graded.
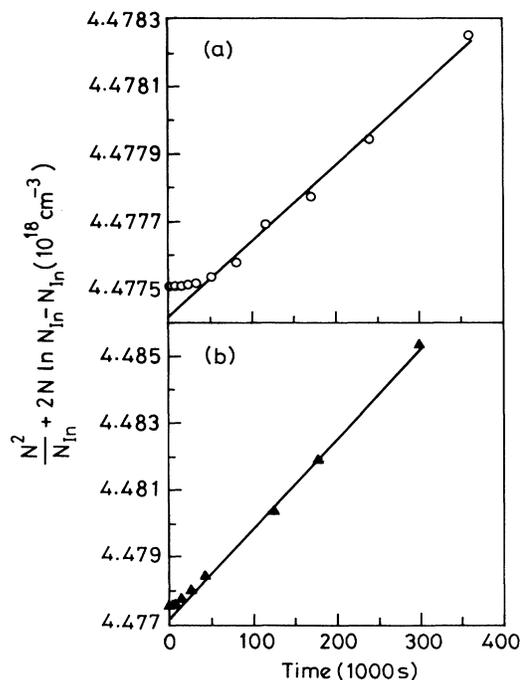

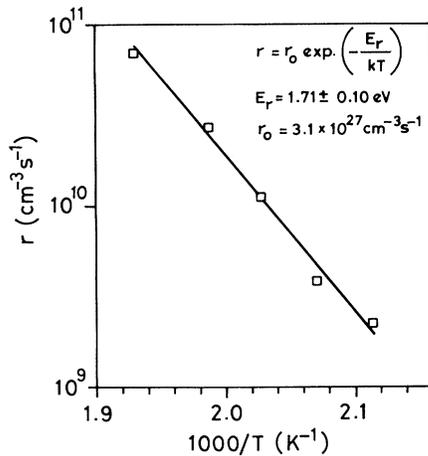FIG. 3. Analysis of annealing kinetics based on Eqs. (2) and (3) for (a) 200 °C and (b) 230 °C.

FIG. 4. Arrhenius plot of the annealing parameter r.

The reactivation of near-surface acceptors is accompanied by passivation in the interior of the bulk (at depths greater than 2.4 μm). This points to the in-diffusion of hydrogen. This migration is possibly aided by a small drift electric field which is present due to the concentration gradient of active acceptors. In order to check the existence of a diffusion process, we plot in Fig. 5 the depth of passivation (d) as a function of $t^{0.5}$ following the relation

$$d = (D_{\text{eff}} t)^{0.5} \tag{5}$$

which explains a normal diffusion process.[1] Here D_{eff} denotes the effective diffusion coefficient of H in InP in the presence of trapping at dopant sites and is obtained from the slope of least-square fitted lines in Fig. 5. The depth of passivation is taken as the depth at which the active acceptor concentration is one half of the bulk value. The plot reveals that a diffusion process exists for shorter annealing times. The deviation from Eq. (5) as time progresses points to a gradual transformation of the

reactivation mechanism from diffusion limited to H_2 molecule formation limited. Figure 6 shows the Arrhenius plot for D_{eff} which follows the relation

$$D_{\text{eff}}(T) = 0.57 \exp \left[\frac{-(1.13 \pm 0.10) \text{ eV}}{kT} \right] . \tag{6}$$

It should be noted that the D_{eff} differs from the actual diffusion coefficient of H in the material depending on the concentrations of acceptor traps and the surface H.

The existence of the diffusion process in the present case is clearly the cause for the deviation of the reactivation kinetics from the model of ZW during shorter annealing times. The presence of diffusion enhances the reactivation of acceptors more than that which can be accounted for by the H_2 formation alone. The deviation can also be understood by considering the fact that in the presence of diffusion, the time rate of change of the total hydrogen concentration at a given position, which is the sum of [AH], [H], and 2[H_2], is not equal to zero. The quantity [H_2] refers to the concentration of H_2 molecules. On the other hand, the model of ZW requires that the condition $\partial[H_T]/\partial t = 0$ is satisfied. In the event that the above condition is not satisfied, a simple analysis leading to Eqs. (2) and (3) is not possible. As time progresses, the ability of H to diffuse decreases due to a reduced concentration gradient and the associated electric field. Hence $\partial[H_T]/\partial t \rightarrow 0$ and the data obeys the model of ZW for longer annealing times. As the annealing temperature is increased, the thermally activated diffusion process would quickly lead to flatter acceptor profiles so that the molecule formation regime is reached sooner.

This study points to the fact that the very presence of a concentration gradient of dopants after hydrogenation would lead (during annealing) to a H diffusion process to begin with, before the H_2 molecule formation process takes over to decide the reactivation kinetics. However, the observation of these two processes would depend upon the external parameters such as annealing temperatures and measurement time scales.
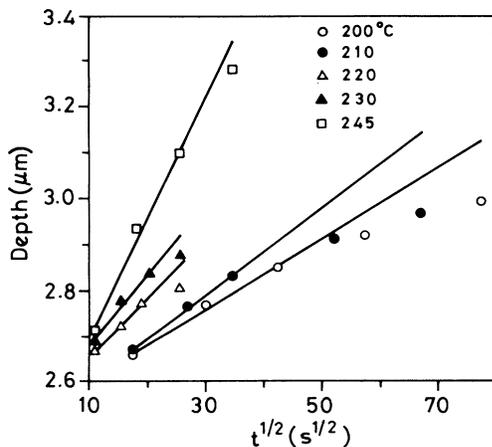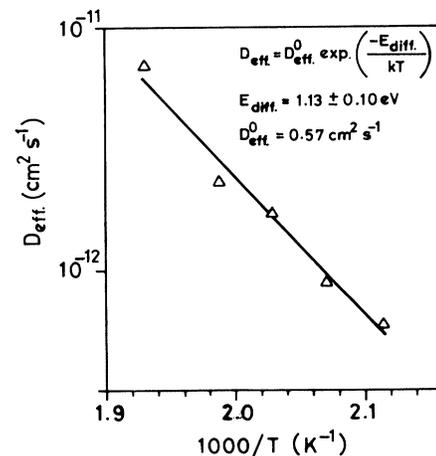

FIG. 5. Passivation depth as a function of the square root of annealing time for different annealing temperatures. The depth considered is where the acceptor concentration is one-half of the bulk value.

FIG. 6. Arrhenius plot of the effective diffusion coefficient D_{eff}.

IV. SUMMARY

We have studied the reactivation mechanisms of the hydrogenated acceptors in p-InP during unbiased annealing. The reactivation does not follow first-order kinetics in contrast to that during annealing under a reverse bias. The reactivation slows down gradually with annealing time and this is attributed to substantial retrapping of H at the acceptor sites in the same region of the sample. For shorter annealing times, the concentration profiles point to acceptor passivation by H in the bulk while the near surface acceptors get reactivated. This is correlated to the in-diffusion of H as the passivation depth varies as $t^{0.5}$. As the diffusion progresses, the gradient of the acceptor concentration and hence the electric field decreases and this reduces H migration into the bulk. As a result, retrapping of H in the same region increases and this is manifested as the continuously reducing reactivation efficiency.

As the annealing time increases further, the in-diffusion becomes less efficient such that the removal of thermally liberated H to reactivate acceptors is most likely determined by the H_2 molecule formation process alone. The existence of this mechanism for longer times is revealed by the fit of the kinetic data in the H_2 molecule formation model of ZW.[15] The concentration profiles and the kinetics data suggest a gradual transformation of the reactivation process from a diffusion limited to a H_2 molecule formation limited process.

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