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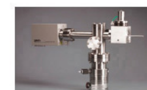
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Influence of CH_4/H_2 reactive ion etching on the deep levels of Si-doped $Al_xGa_{1-x}As$ (x=0.25)*

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We study the passivation and recovery of shallow and deep levels in Si-doped AlGaAs exposed to CH_4/H_2 and H_2 reactive ion etching (RIE). The carrier concentration depth profile is determined by capacitance–voltage measurements. The activation energy to recover the silicon donors is found to be 1.1 eV for samples exposed to CH_4/H_2 RIE and 1.3 eV for samples exposed to H_2 RIE. We study the behavior of *DX* centers in Si-doped AlGaAs layers after RIE exposure and subsequent thermal annealing by using deep level transient spectroscopy. For CH_4/H_2 RIE a new emission is detected at the high temperature side. We identify this emission as the *DX*3 center, which is assigned to a *DX* center with three aluminum atoms surrounding the Si donor. This *DX* center is only detected on the samples exposed to CH_4/H_2 RIE. We explain the formation of this deep level to the highly selective removal of Ga atoms in favor of Al atoms. Consequently Al-rich regions are created near the surface. © *1996 American Vacuum Society.*

I. INTRODUCTION

The incorporation of atomic hydrogen can cause significant changes in the electrical properties of III–V compound semiconductors. The passivation of shallow and deep levels results from the formation of complex radicals between hydrogen and donors or acceptors, as well as the annihilation of dangling bonds and defects by hydrogen.[1,2] Pearton and co-workers[3] have studied the effect of plasma hydrogenation on different shallow levels in GaAs and AlGaAs. They observed that Si, Ge, Sr, S, Se, and Te are passivated by hydrogen. The depth of passivation is determined by the hydrogen diffusion, which is inversely proportional to the dopant concentration. They observed that the shallow acceptors Be, Mg, Zn, and Cd in GaAs are not affected by hydrogenation, with the exception of Si acceptors in AlGaAs, which showed a strong passivation. The formation of Si–H bonds correlated with the neutralization of the shallow levels has been identified by infrared absorption spectroscopy in hydrogenated Si-doped GaAs, for both p and n type.[4,5] Detailed theoretical calculations have been carried out by Pavesi,[6,7] studying the presence of hydrogen in undoped and doped GaAs, based on first-principles calculations in the local density approximation within a supercell approach. He found that the stable configuration for the H-donor complex in GaAs is an antibonding donor site, and for the H-acceptor complex is a site along the bond near the bond center. In both cases, lattice relaxation is necessary to obtain the passivation of the impurities. Different charge states of hydrogen in GaAs have been identified,[8–10] having either acceptor or donor deep level characteristics, which depend on the dominant shallow level.

Initially, Pearton and co-workers[3] showed that the activation energy for recovery of the donor electrical activity was around 2.1 eV for each of the different dopant species (Si, Ge, Sn, S, Se, and Te), but varied as the strength of an isolated hydrogen-donor species bond. Their results were obtained from Hall measurements on samples annealed at different temperatures. The activation energy for recovery of the donor electrical activity obeys the first-order kinetics assuming only the dissociation of hydrogen-donor complexes. Cho and co-workers[11] have shown that the dissociation of the hydrogen–silicon donor complexes can be enhanced by the presence of an electric field and in this case the donor reactivation can be obtained at lower temperatures. Zundel[12] has shown that conventional annealing experiments in the absence of an electric field tend to overestimate the thermal stability of dopant-H pairs because of the presence of significant reassociation of these charged species. Roos and co-workers[13] have studied the thermal dissociation of Si–H complexes under high electric field. They have measured a dissociation energy of (1.2×0.1) eV and a dissociation attempt frequency of 6.3×10^7 s^{-1}. Also they suggested that hydrogen can diffuse in n-type GaAs as a negatively charged species H^-. The same procedure was repeated by Pearton and co-workers[14] and they obtained similar results. Modeling the hydrogen diffusion in GaAs, Morrow[15] showed that the dissociation energy of hydrogen-shallow defect complexes decreases from 2.1 eV to zero with increasing hydrogen concentration or defect concentration. From this result, one would expect that the recovery activation energy is dependent on the plasma conditions, exposure time, and reactor design.[2,3,16–19]

The effect of hydrogen plasma exposure on deep levels present in GaAs and AlGaAs has also been studied by deep level transient spectroscopy (DLTS).[20–22] Dautremont-Smith[20] observed that, for GaAs after plasma exposure, donors and deep levels were passivated. The donors were recovered after annealing at 400 °C, while deep levels were

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still passivated for temperatures below 600 °C. Essentially, this effect comes from the fact that the deep levels in GaAs are related to crystal imperfections or residual impurities originating from the growth conditions.[23] In the case of Al–GaAs, the nature of the deep level is directly related to the donor atom itself.[24–26] This effect causes a strong lattice relaxation accompanied by bond breaking of the donor atom. This deep level is the so-called *DX* center. The structural rearrangement induced by the formation of the *DX* center will also be dependent on the configuration of the neighboring atoms around the silicon donor transformed in the deep level. Different local configurations of gallium and aluminum atoms around the silicon donor will form different deep levels. For an aluminum concentration lower than 22% the *DX* center level is situated in the conduction band. For higher aluminum concentration, the *DX* center has a stable position in the band gap.

The passivation of the *DX* centers is believed to proceed via the formation of *DX*–H complexes.[27] It has been found that the stable position of hydrogen is the antibonding position of the silicon atom in the *DX* center, independent of the surrounding aluminum. This process is in fact similar to the passivation of silicon donors. Nabity and co-workers[22] measured 2.0 eV as the activation energy for the recovery of the *DX* centers, which is comparable to the activation energy of the silicon donors (2.1 eV).

The effect of reactive ion etching (RIE) on GaAs and AlGaAs in mixtures of hydrocarbons (CH_4 and C_2H_6) and hydrogen has been shown to behave as a hydrogenation process.[16–18,28–34] This is due to the relatively low hydrocarbon concentration (15%–25%) normally used, making hydrogen the predominant specimen in the plasma. The donor reactivation can be obtained after annealing temperatures around 400 °C,[16–18,28,30] and it follows the same kinetics as observed for hydrogenation. It is important to mention that to our knowledge, deep levels introduced by methyl radicals in the plasma have not been identified before.

In this article we study the passivation and recovery of shallow and deep levels in Si-doped AlGaAs exposed to CH_4/H_2 RIE. In Sec. III A we discuss the recovery kinetics of Si donors in AlGaAs layers. In Sec. III B we study the behavior of *DX* centers in Si-doped AlGaAs layers after RIE exposure and subsequent thermal annealing by using deep level transient spectroscopy (DLTS). We compare CH_4/H_2 RIE with H_2 RIE in order to extract the effect of the addition of CH_4 in the gas mixture.

In Sec. IV we summarize the conclusions.

II. EXPERIMENT

The passivation and recovery of Si-doped AlGaAs (25% Al) exposed to CH_4/H_2 and H_2 RIE are studied by deducing the carrier concentration from capacitance–voltage ($C-V$) measurements on metal–AlGaAs Schottky diodes. The AlGaAs layers were grown on a semi-insulating GaAs substrate by molecular beam epitaxy (MBE). A sequence of a 1-μm-thick undoped AlGaAs buffer layer, followed by 2000 Å Si-doped AlGaAs layer, and a 200 Å undoped GaAs cap layer was grown. Before RIE exposure the diode areas are defined by photolithography and AuGe:Ni/Au is used as the ohmic contact. The samples are exposed to CH_4/H_2 RIE conditions defined as follows: 15% CH_4 in H_2, a dc self-bias of −310 V, a pressure of 36 mTorr, and a total gas flow of 75 sccm. All the plasma exposures are carried out at room temperature. The samples are etched for 5 min in order to remove the undoped GaAs cap layer. Thermal treatments are done between 250 and 550 °C using a halogen lamp rapid thermal annealing system in a forming gas ambient (90% N_2, 10% H_2). For comparison, H_2 RIE has been done using the same power density. In this case a lower dc self-bias (−260 V) is measured during the RIE process. Before H_2 RIE exposure, the samples are etched in a solution of H_2SO_4;H_2O_2;H_2O (1;8;1000) with a calibrated etch rate of 400 Å/min to remove the undoped GaAs cap layer. This procedure is also used for the preparation of the nonplasma exposed reference samples. $C-V$ measurements are performed using a 4275 Hewlett–Packard LCR analyzer. The dimensions of our diodes are measured to be $30\times92\ \mu m^2$ by scanning electron microscopy.

The kinetics of *DX* centers passivation and recovery in Si-doped $Al_{0.25}Ga_{0.75}As$ exposed to CH_4/H_2 and H_2 RIE submitted to different annealing temperatures are studied by DLTS. Capacitance DLTS has been performed in a DMC DLS-82E system by using a rate window of 100 Hz, pulse width of 500 μs, reverse bias of −1 V, and forward bias of 0.5 V. The measurements are carried out between 77 and 293 K, with the samples mounted on TO 5 holders. The temperature is measured by a thermocouple beside the sample holder. The warm up rate is around 1 K/min. The thermal activation energies and the capture cross section are obtained by taking the temperature of the maximum emission at different frequencies. For these measurements, the frequencies are 100, 250, 500, and 1000 Hz. The deep level (or trap) concentration N_T, is estimated by

$$N_T=2(N_D-N_A)\frac{\Delta C}{C_0}, \tag{1}$$

where ΔC is measured from the peak height, C_0 is the initial capacitance of the diode under reverse bias, and N_D-N_A is the free carrier concentration obtained from the $C-V$ measurements. This equation is the well-known Lang's formula. It is valid only for $N_T \ll N_D-N_A$.

III. RESULTS AND DISCUSSIONS

A. Recovery kinetics of Si donors in $Al_{0.25}Ga_{0.75}As$ after CH_4/H_2 and H_2 RIE

It is well accepted that the passivation of the Si donor in GaAs is due to the formation of silicon–hydrogen bonds,[2,3,7,11,28,35] involving the electron which was donated to the conduction band. The electrical reactivation of the silicon donors can be obtained after thermal treatments at temperatures higher than 400 °C. The kinetic mechanism of

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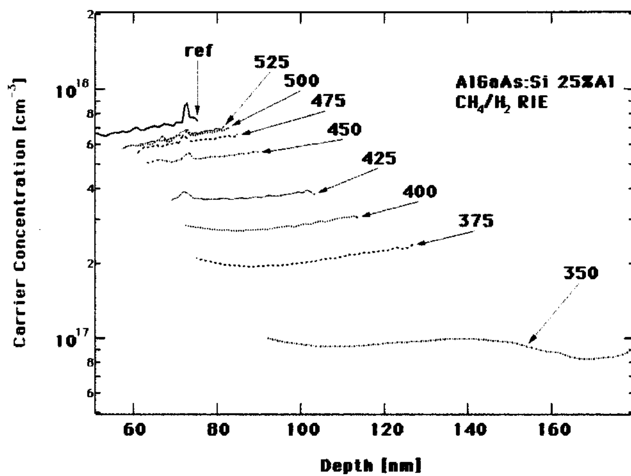

FIG. 1. Carrier concentration depth profile obtained by $C-V$ measurements as a function of annealing temperature after CH_4/H_2 RIE.

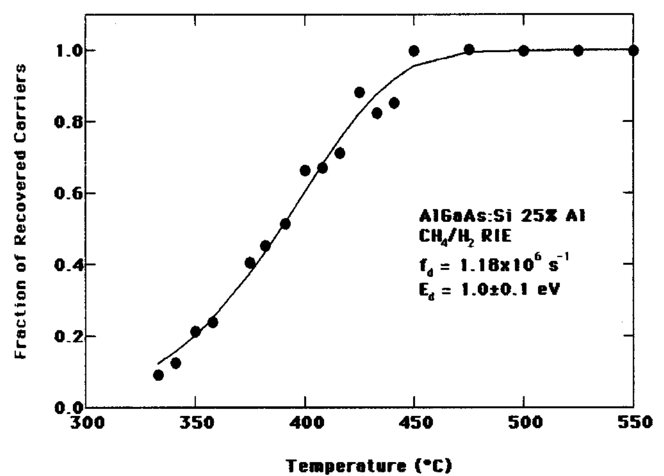

FIG. 2. Fraction of recovered carrier concentration (N_d/N_0) of Si-doped AlGaAs exposed to CH_4/H_2 RIE as a function of annealing temperature. The dots are the experimental data and the line is the model fitting (Ref. 35). The activation energy (E_d) and the dissociation attempt frequency (f_d) are 1.0 $\pm$0.1 eV and 1.18×10^6 s^{-1}, respectively.

this process is based on the dissociation of the silicon–hydrogen bond, which follows the first-order kinetics as proposed by Chevallier:[35]

$$\frac{N_d}{N_0}=1-\exp\left[-tf_d\exp\left(-\frac{E_d}{kT}\right)\right], \tag{2}$$

where N_d/N_0 is the fraction of recovered donors, t is the annealing time (s), f_d is the frequency of Si–H bond dissociation attempts (s^{-1}), T is the annealing temperature (K), and E_d is the dissociation energy (eV). Pearton and co-workers[3] have studied the neutralization properties of hydrogen as a function of the donor species in GaAs and AlGaAs. They found that the passivation mechanism was associated with the bond strength of the donor species to hydrogen, and that the dissociation energies were dependent on the donor element. In their experiments, the samples were exposed to the H_2 plasma for a long time (30 min) at a high temperature (250 °C). The electrical reactivation of silicon donors in GaAs exposed to CH_4/H_2 RIE has also been studied by Collot[28] and Cameron.[16] Collot's experimental results were in agreement with a dissociation energy between 1.7 and 1.8 eV and a dissociation attempt frequency of 10^{13} s^{-1}. On the other hand, Cameron has not found good agreement between his experimental data and the fitting parameters (dissociation frequency and energy) as obtained by Chevallier and co-workers.[35] His results show the same error as observed for the calculations of the dissociation energies of donors–H in n-type GaAs. In fact, the reassociation of donor–H complexes has never been considered in the calculations mentioned above.

We have studied the carrier depth profile in Si-doped AlGaAs layers as a function of annealing temperature after CH_4/H_2 and H_2 RIE exposures. Figure 1 shows the carrier profile obtained by $C-V$ measurements for the samples exposed to CH_4/H_2 RIE. It can be seen that the carrier concentration increases with annealing temperature. Using the depth averaged values for the carrier concentration for each annealing temperature, we estimated the activation energy for recovery of the silicon donors, based on the first-order kinetics proposed by Chevallier.[35] Figures 2 and 3 show the fitting of this model to our experimental data for the samples exposed to CH_4/H_2 and H_2 RIE, respectively. The activation energies and dissociation frequencies were found to be (1.0$\pm$0.1) eV and 1.2×10^6 s^{-1} for CH_4/H_2 and (1.3$\pm$0.1) eV and 1.0×10^7 s^{-1} for H_2 RIE. These values are comparable to those obtained by the other authors[13,14] using biased diodes. In our case we have not applied any electric field but our samples were annealed with Schottky metal on top. We believe that the electric field created by the metal–semiconductor junc-

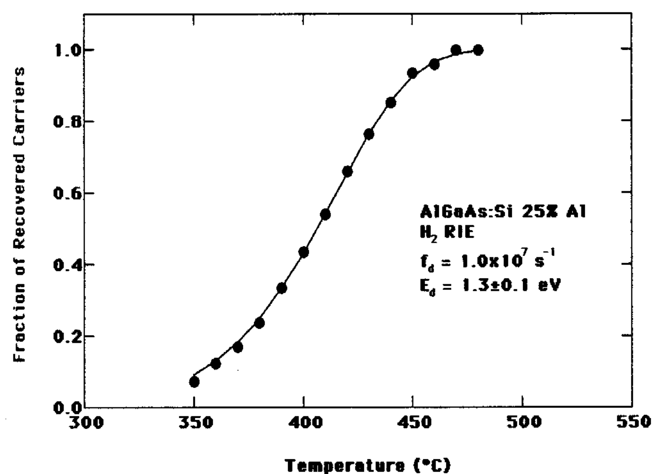

FIG. 3. Fraction of recovered carrier concentration (N_d/N_0) of Si-doped AlGaAs exposed to H_2 RIE as a function of annealing temperature. The dots are the experimental data and the line is the model fitting (Ref. 35). The activation energy (E_d) and the dissociation attempt frequency (f_d) are 1.3 $\pm$0.1 eV and 1.0×10^7 s^{-1}, respectively.

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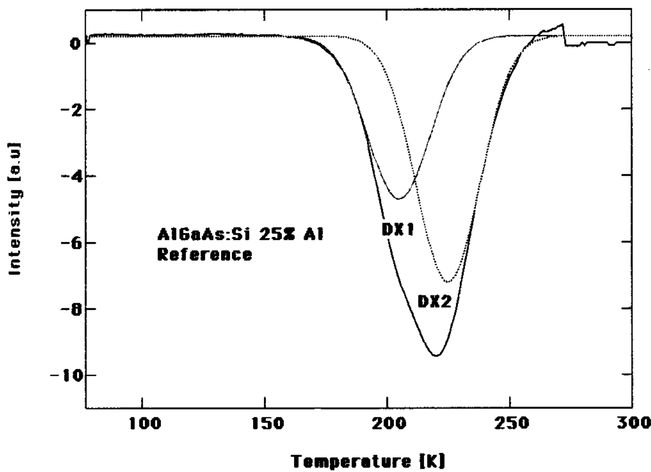

FIG. 4. DLTS spectrum of Si-doped AlGaAs sample ($N_D=7\times10^{17}$ cm^{-3}). The deconvoluted peaks are obtained by fitting to Gaussian curves.

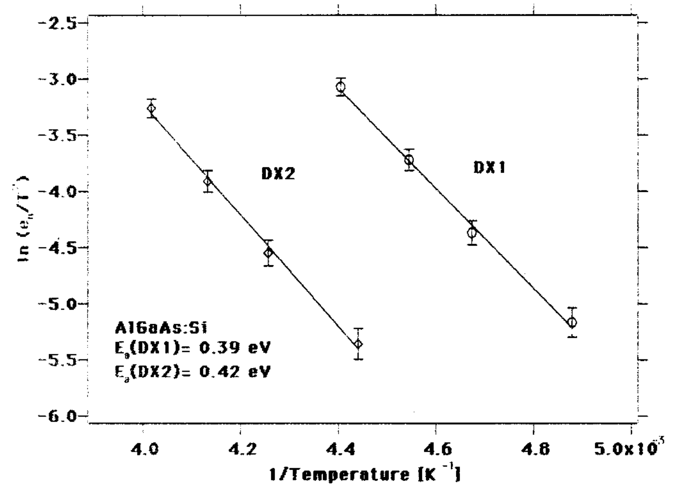

FIG. 5. Arrhenius plot of $DX1$ and $DX2$ emissions. The thermal activation energies and the capture cross sections are 0.39 eV and 5.2×10^{-14} cm^{-2} for $DX1$, and 0.42 eV and 4.1×10^{-14} cm^{-2} for $DX2$.

tion can influence the kinetics of Si–H complex dissociation. Morrow[15] has shown that the activation energy for hydrogen diffusion in Si-doped GaAs and the dissociation energies of hydrogen-defect complexes are dependent on the concentration of hydrogen. Also, hydrogen has been found to diffuse deep into GaAs when plasma exposure is done at high temperature and at long times. Our results show that H_2 RIE has a higher activation energy and dissociation attempt frequency than CH_4/H_2 RIE. This could be due to the fact that hydrogen diffuses deeper for H_2 compared to CH_4/H_2 RIE.

The dissociation frequencies obtained from our data (10^6–10^7 s^{-1}) are comparable with the values obtained by Roos[13] but orders of magnitude lower than the values (10^{13}–10^{14} s^{-1}) obtained by Pearton.[14] This behavior suggests that the donor recovery and hydrogen outdiffusion involve a more complicated process[36,37] than the dissociation and recombination of Si–H complexes. The existence of a multistep reaction sequence can significantly alter the thermodynamic process. In our case, this could be explained by the dissociation of Si_{Ga}–H complexes and the formation of hydrogen molecules. The combination of these reactions can explain the effective activation energy and dissociation attempt frequency observed our experiments.

B. Donor deep level (*DX* center) behavior after CH_4/H_2 and H_2 RIE exposure and subsequent thermal annealing

1. DLTS spectra and activation energies: Reference samples

Figure 4 shows a typical DLTS spectrum for Si-doped $Al_{0.25}Ga_{0.75}As$ reference samples. This spectrum shows a broad and asymmetric emission, where we can clearly resolve two different emission peaks centered at 200 and 220 K. The spectral deconvolution is done by considering a Gaussian approximation for the deep level emission. These two emissions are in agreement with the results published by Mooney and co-workers[38,39] for the deep levels in AlGaAs with the same aluminum concentration. They attributed the first emission, $DX1$, to the DX center having one aluminum atom neighboring the silicon donor involved in the formation of the deep level, and the other, $DX2$, two aluminum atoms. The thermal activation energies and capture cross sections of these deep levels are obtained from an Arrhenius plot of $\ln(e_n/T^2)$ against $1/kT$ (Fig. 5), where e_n is the emission rate, T is the temperature corresponding to the maximum deep level emission, and k is the Boltzmann constant. The values of thermal activation energies and capture cross sections are 0.39 eV and 5.2×10^{14} cm^{-2} for $DX1$, and 0.42 eV and 4.1×10^{14} cm^{-2} for $DX2$.

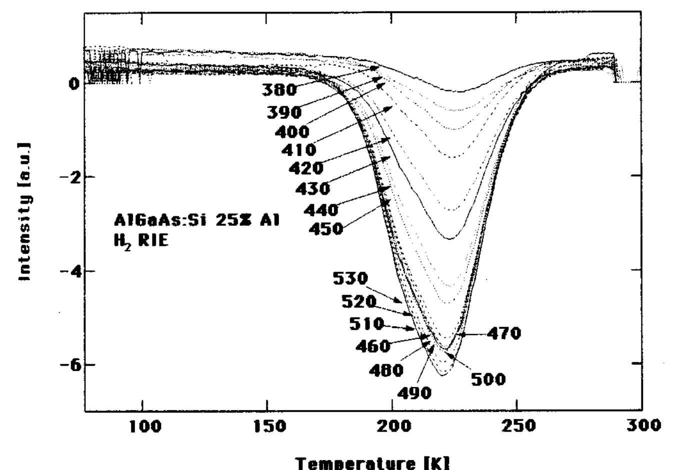

FIG. 6. The annealing temperature dependence of DX center emission in Si-doped AlGaAs samples exposed to H_2 RIE. The annealing temperature is varied from 380 to 530 °C.

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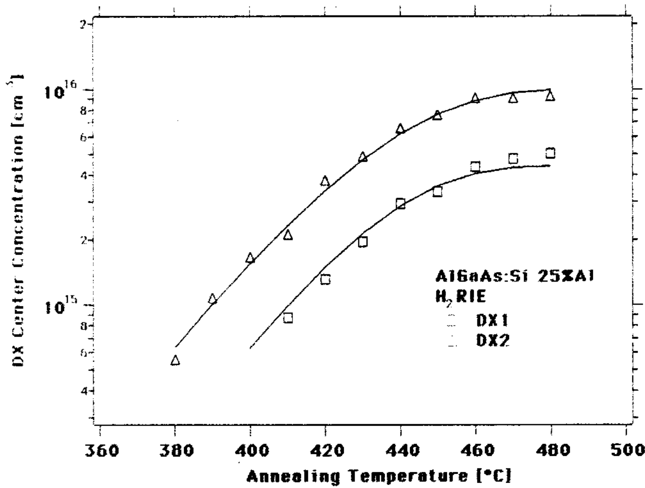


FIG. 7. The annealing temperature dependence of the $DX1$ and $DX2$ center concentration of Si-doped AlGaAs exposed to H_2 RIE. The solid line is the model fitting (Ref. 35).

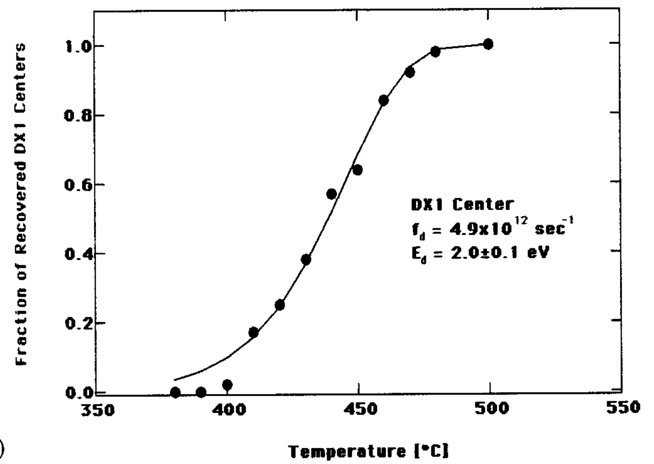
2. Annealing temperature dependence of DX centers in Si-doped AlGaAs exposed to H_2 RIE

Figure 6 shows the temperature dependence of DX center emission in Si-doped AlGaAs exposed to H_2 RIE. For samples annealed at temperatures lower than 380 °C, the emission was below the detection limit. The DLTS emission intensities increase with increasing annealing temperature and complete recovery is reached for temperatures higher than 470 °C. In the temperature range where the DX center emission can be detected two emissions are resolved, similar to the reference sample. The DX center concentrations are estimated by using Lang's formula [Eq. (1)].

Figure 7 shows the annealing temperature dependence of the $DX1$ and $DX2$ concentrations. From these data, we calculate the activation energies to recover the DX centers based on the first-order approximation [Eq. (2)]. Figures 8(a) and 8(b) show the fitting between the experimental and theoretical data for $DX1$ and $DX2$ centers. The activation energy to recover the DX centers and the dissociation attempt frequency of DX–H complexes are (2.0 ± 0.1) eV and 4.9×10^{12} s^{-1} for $DX1$, and (1.8 ± 0.1) eV and 1.7×10^{11} s^{-1} for $DX2$. Our results of activation energies are quite comparable to the values obtained by Nabity[22] (2.1 eV). However, the dissociation attempt frequencies of DX–H for both DX centers, are lower than their values (1×10^{14} s^{-1}). This discrepancy can be caused by differences in the hydrogenation process and also by the scattering of their experimental data.

3. Annealing temperature dependence of DX centers in Si-doped AlGaAs exposed to CH_4/H_2 RIE

Figure 9 shows the temperature dependence of DX center emission in Si-doped AlGaAs exposed to CH_4/H_2 RIE. The evolution of the emission recovery is quite comparable to the samples exposed to H_2 RIE. The DX center remains fully passivated for annealing temperatures lower than 350 °C. Complete recovery is reached at 450 °C. In addition to the



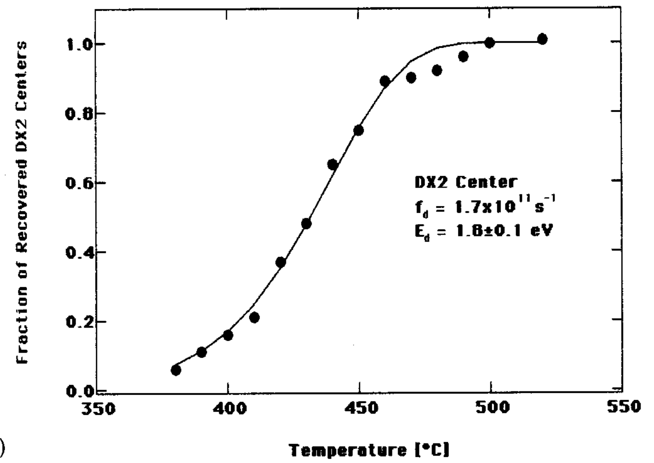


FIG. 8. (a) and (b) Fraction of recovered $DX1$ (a) and $DX2$ (b) centers from AlGaAs exposed to H_2 RIE. The dots are the experimental data and the lines are the fitting with the model proposed by Chevallier (Ref. 35).

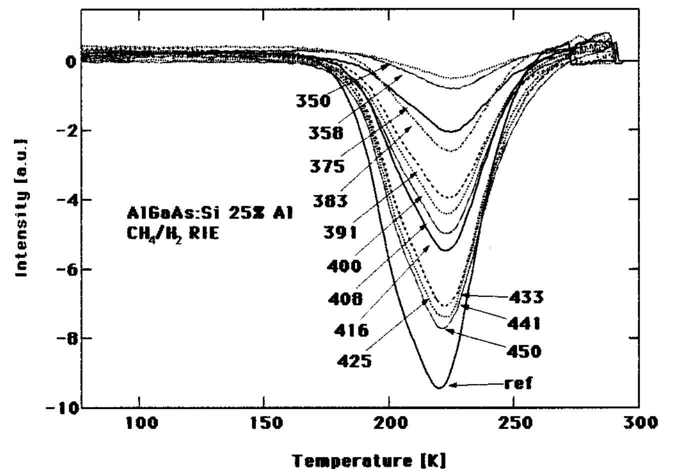


FIG. 9. The dependence of the DX center emission on the annealing temperature in Si-doped AlGaAs exposed to CH_4/H_2 RIE. The annealing temperature is varied from 350 to 450 °C.

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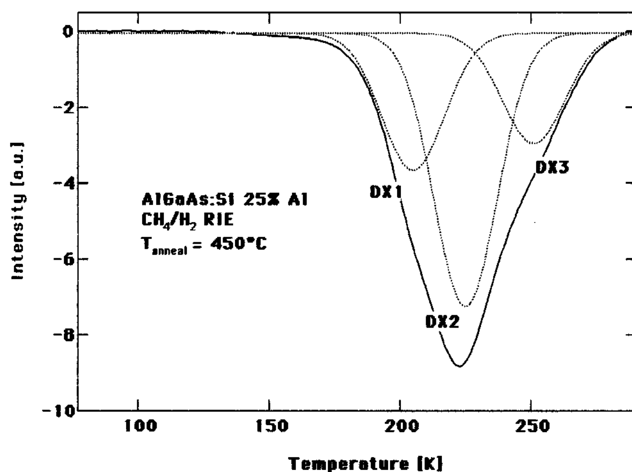

FIG. 10. DLTS spectrum of Si-doped AlGaAs exposed to CH_4/H_2 RIE and annealed at 450 °C. The deconvoluted peaks are obtained by fitting to Gaussian curves. The thermal activation energy of the *DX*3 center is 0.47 eV and the capture cross section is 1.2×10^{-14} cm^{-2}.

two emissions observed for the reference samples, *DX*1 and *DX*2, a third emission is observed as a shoulder at the high temperature side. Figure 10 shows the DLTS emission spectrum of the samples annealed at 450 °C after deconvolution. The thermal activation energy of this emission is estimated by the Arrhenius plot as 0.47 eV with a capture cross section of 1.2×10^{-14} cm^2. The thermal activation energy of this new emission is equal to the *DXD* emission observed by Baba,[40] which he associated to the *DX* center where the local environment surrounding the silicon donor is mainly composed of aluminum atoms. We believe that this emission is associated to the *DX* center where the silicon donor is surrounded by three aluminum atoms as proposed by Morgan's model.[41] The position of this emission is close to the position of the shoulders observed by Mooney and co-workers.[38,39] For this reason, this emission is labeled as *DX*3.

As morgan's model[41] states that this emission can be detected only for high aluminum concentration, and this emission is not observed for the reference samples and samples exposed to H_2 RIE, the presence of this emission can only be related to the damage induced by the CH_4/H_2 RIE process. This can be explained by the more effective removal of the gallium compared to the aluminum atoms during RIE. This is supported by the fact that the etch rate is strongly decreased with increasing aluminum concentration. The presence of aluminum-rich regions near the surface giving rise to the formation of these *DX* centers can be expected.

We evaluated the annealing temperature dependence of the density of the three different *DX* centers: *DX*1, *DX*2, and *DX*3. The activation energy to recover the DX centers and dissociation attempt frequencies of the *DX*–H bond are (1.9 ± 0.1) eV and 2.3×10^{12} s^{-1} for *DX*1, (1.8 ± 0.1) eV and 3.5×10^{11} s^{-1} for *DX*2, and (1.9 ± 0.1) eV and 3.1×10^{12} s^{-1} for *DX*3. The activation energies and dissociation attempt frequencies obtained for *DX*1 and *DX*2 are comparable to the values obtained for the samples exposed to H_2 RIE.

On the other hand, we still observe a large difference between our values obtained for the *DX* centers and the shallow levels independent of the hydrogenation process (H_2 or CH_4/H_2 RIE). Since the formation of Si–H complexes involves the capture of one electron from the silicon donor, the two electrons captured in the *DX* center will increase the probability to keep silicon bound to hydrogen. Also, the reactivation of silicon donors can be better explained by a multistep reaction process which can involve the formation of hydrogen molecules or its capture by the deep levels.

IV. CONCLUSIONS

In this article we studied the passivation and recovery of shallow and deep levels in Si-doped $Al_{0.25}Ga_{0.75}As$ exposed to CH_4/H_2 and H_2 RIE. We evaluated the recovery kinetics of Si donors in $Al_{0.25}Ga_{0.75}As$ after CH_4/H_2 RIE and subsequent thermal annealing by $C-V$ measurements. The activation energies to recover the Si donors were found to be 1.1 and 1.3 eV for CH_4/H_2 and H_2 RIE, respectively. We assume that the difference is related to the differences in the hydrogenation process. The dissociation attempt frequencies were found to be 1.2×10^6 and 1.0×10^7 s^{-1} for CH_4/H_2 and H_2 RIE, respectively. These values are much lower than the expected values (10^{13}–10^{14} s^{-1}) for a thermal dissociation process. This behavior suggests that the donor recovery and hydrogen outdiffusion involve a more complicated process than a simple dissociation. This could be explained by considering the reassociation of Si–H complexes and the formation of H_2 molecules during hydrogen outdiffusion.

We evaluated the recovery kinetics of *DX* centers in Si-doped $Al_{0.25}Ga_{0.75}As$ exposed to H_2 and CH_4/H_2 RIE and subsequent thermal annealing by DLTS. For the H_2 RIE exposed samples two emissions were observed which were attributed to *DX*1 and *DX*2 centers. These peaks were resolved by considering a Gaussian approach. We considered the multilevel structure of *DX* centers extracted from the deconvoluted spectra, usually not taken into account by other authors. We determined the thermal activation energies as 0.39 and 0.42 eV for the *DX*1 and *DX*2 centers, respectively. The activation energies to recover these *DX* centers were found to be 1.9 and 1.8 eV for the *DX*1 and *DX*2 centers. The dissociation attempt frequencies were found to be 4.9×10^{12} and 1.7×10^{11} s^{-1} for *DX*1 and *DX*2 centers, respectively. These are low compared to the expected values. Once more we believe that this feature is related to the hydrogenation process and different kinetics to recover the *DX* centers. The *DX* centers were completely recovered after annealing at 450 °C. For the CH_4/H_2 RIE exposed samples, we observed the presence of a new deep level at the high temperature side with thermal activation energy of 0.47 eV. We attributed this deep level to the *DX*3 center. The atomic configuration of this *DX* center is formed by three Al atoms surrounding the Si donor. The probability to observe this *DX* center is very low considering the Al concentration of our samples (25%). The formation of this *DX* center is due to the high selectivity of the RIE in the removal of Ga atoms com-

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pared to Al atoms. Consequently Al-rich regions will be created near the surface. This is the first time that such an effect is observed.

Comparing the activation energies and the dissociation attempt frequencies of the Si donors and the *DX* centers we concluded that both processes are governed by different kinetic mechanisms. Although the *DX* center is originated from the Si donor, the atomic configuration of the deep level involves electron capture, large lattice relaxation, and bond breaking which can play an important role in the recovery mechanism of *DX* centers.

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