Mechanisms of Impurity Deactivation in GaAs during Reactive Ion Etching

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The cause of carrier removal in GaAs due to plasma processing is found to consist of two mechanisms from a photoreflectance depth-profiling study. In the close vicinity of the surface, the Fermi level is pinned by the defects created by ion bombardment. In a much deeper region, electrical passivation of doped impurities themselves is playing the dominant role. Secondary-ion mass analysis confirmed that hydrogen diffusion is indeed responsible for the latter process. We suggest that the physically damaged surface layer acts as a sponge for even a trace amount of hydrogen in the processing environment. [S0031-9007(96)01480-9]

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Dry etching techniques such as reactive ion etching (RIE) are widely used in fabricating modern semiconductor devices down to submicron scale of devices. The superiority of the technique stems from extremely high definition of the etched patterns. This otherwise excellent processing technique has one essential drawback, namely, the carrier removal in the vicinity of the surface at the depth exceeding by even an order of magnitude the projected range of the impinging energetic ions. Despite several careful studies of the impurity deactivation process [1–3], the physical mechanism of the material degradation has not been clarified yet. In particular, the most puzzling is the impurity deactivation at the depth far exceeding a physical damage caused by the etching plasma [1]. A most plausible cause could be a fast (recombination enhanced?) diffusion of the yet unknown species, likely passivating the electrically active impurities. Understanding the physical mechanism of the impurity deactivation process is essential for further progress in the RIE technology, which until today has been mostly purely phenomenological.

It is most likely that the deactivation processes in a close vicinity of the surface (within the projected range of the impinging ions) differ drastically from the process at the larger depths. It is well known that native defects are produced by ion bombardment. It has been found that even modest damage causes the Fermi-level pinning [4]. Native defects, which are generated by atomic displacements near the surface, act as deep acceptors (donors) in n-type (p-type) semiconductors. Thus the electrically active dopants become charge compensated by the damage-induced defects. The Fermi-level stabilization is achieved because the native defects in GaAs generated by the ion bombardment act as electrically amphoteric impurities [4]. It should also be mentioned some native defect pairs in GaAs may behave as negative-U centers which also cause Fermi-level pinning [5].

The process of carrier removal at the larger depths (100 nm or more) must, however, originate from a completely different mechanism. It is possible that the damaged surface layer enhances diffusion of some impurity/defect that passivates donors or acceptors in the bulk. Such a process is well characterized and understood in the case of hydrogen passivation. Hydrogen atoms, rapidly diffusing into the bulk of semiconductors, become associated with electrically active impurities neutralizing them [6]. This results in the effective removal of the impurity levels from the gap, so the material behaves as less doped. Such an effect is a prime suspect in the case when an etchant gas contains hydrogen, but the occurrence of carrier removal in the bulk has also been reported for nominally hydrogen-free systems [7].

Standard methods, such as C-V profiling or spread resistance, were previously used to show the conversion of an otherwise homogeneously doped semiconductor to an i/n junction. They cannot, however, provide unambiguous information about the significance and relative role of the carrier deactivation mechanisms outlined above. To obtain information on the nature of this i region, a different approach is necessary.

In this study, we used photoreflectance (PR) spectroscopy [8] combined with the step-etch method. The technique probes the variation of surface electric field as the wet-etched surface traverses through the damage-introduced layer. This, in turn, provides direct information on whether the deactivation at a certain depth is a compensation (effective carrier removal) or a passivation (effective impurity removal). We have found two mechanisms involved, depending on depth from the surface: a defect-induced Fermi-level pinning was found near the surface, while the passivation of dopant impurities dominates in the deeper region.

The samples were *n*-type GaAs wafers, having a donor concentration of 1.7×10^{17} cm^{-3}, grown by the metalorganic vapor-phase epitaxy technique. To study the effect of RIE-induced damage, a 230 nm-thick SiO_2 film was first deposited at 400 °C, and then completely dry etched by the subsequent RIE process. Two types of etchant gases were tested: CHF_3/O_2 (a mixture) and SF_6, both being popular in patterning dielectric films. After completely removing the SiO_2 film, the GaAs surface was kept exposed to the etchant plasma for additional 8 min. An annealing study at 450 °C in N_2 for 30 min was also performed to check the recovery of carriers.

The setup for the PR measurements is a standard one and has been described in our previous publication [9]. Capacitance measurements were also performed by fabricating Al-Schottky diodes. For (wet) step etching, a solution of $H_3PO_4 : H_2O_2H_2O = 4:1:180$ was used. By stripping about 10 nm per step, PR spectrum was repeatedly recorded.

We first checked the carrier profile using the *C*-*V* method. After the RIE, it was found that the depletion layer edges were shifted to much deeper locations. The positions evaluated are about 200 and 160 nm from the surface after the CHF_3/O_2 and SF_6 RIE, respectively. Thus it is indicated that carriers were indeed removed in the near-surface regions. After annealing at 450 °C, the original carrier profiles were completely restored within experimental uncertainty.

The electric field near the surface (of the *i* layer) was evaluated by the photoreflectance measurements. The spectra in Fig. 1, which were recorded at several etching steps, show characteristic Franz-Keldysh oscillations. Their energy periods give the surface electric field F of the depletion region [10]. Our data indicate that the surface field increases as the wet-etching step proceeds. After stripping about 200 nm, the field value no longer changed upon further step etching.

Analysis of PR results is customarily done in the case of a flat doping profile. If the dopant concentration N_d is constant along depth, it can be evaluated using the measured surface electric field as

$$F = \sqrt{(2eV_{\mathrm{bi}}N_d)/\varepsilon_s} \tag{1}$$

with the knowledge of surface Fermi-level position, which is related to the built-in potential V_{bi}. Such an approach has been used in the pioneering work by Wada and Nakanishi [11], who were the first to estimate the concentration of damage-related compensation centers. However, the assumption of a uniform concentration cannot hold in the surface-damaged semiconductors. When the RIE process depletes carriers in the near-surface region, modification of the potential profile is large enough to invalidate the above treatment.

Following the analysis at the beginning of the paper, two limiting cases of the carrier removal are illustrated in Fig. 2. If a large number of point defects compensating electrically active dopants were introduced, the Fermi-level pinning occurs. Therefore, the electric field in the damaged layer should be small. On the other hand, if the dopant impurities are passivated, the *i* layer resembles an intrinsic semiconductor. The electric field can be thus much larger, as illustrated in Fig. 2(b) [12]. In this latter case, the surface potential causes a finite band bending, producing a nonzero and fairly uniform field across the *i* layer.

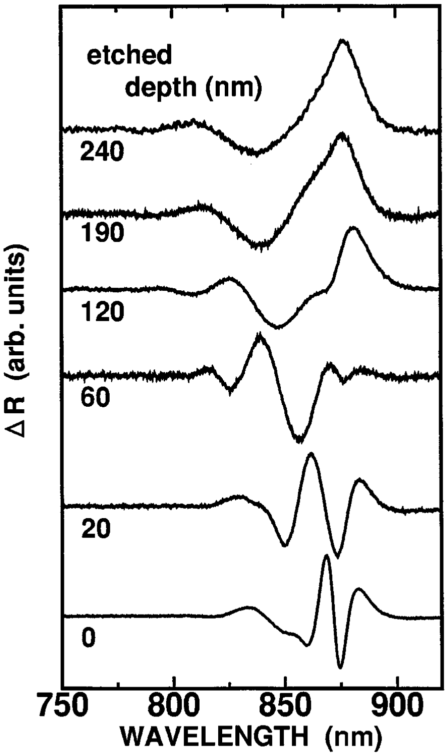

FIG. 1. Photoreflectance spectra for the damage-introduced *n*-GaAs by the RIE with CHF_3/O_2, showing the variation of Franz-Keldysh oscillations as a function of stripped-off layer thickness by the step etching.

These two cases give a totally different variation of the surface electric field as a function of step etching. For small distances from the surface, the electric field should remain small [Fig. 2(a) case], while in the passivated region it should be much larger and uniform [Fig. 2(b)]. Thus the field should increase in an inversely proportional way to the remaining *i*-layer thickness *L*-*d* (see Fig. 2) as it is reduced by the step etching.

Therefore, in Fig. 3 we plot the data in a reciprocal field $1/F$ in order to examine the presence of the passivated region [Fig. 2(b)]. In fact, for the CHF_3/O_2-RIE, a linear variation of $1/F$ as a function of d is clearly seen in the region $50 < d < 190$ nm. The electric field saturates by stripping more than 190 nm since the wet-etched surface now reaches the undamaged *n*-GaAs region. A similar trend is also seen for the SF_6-RIE.

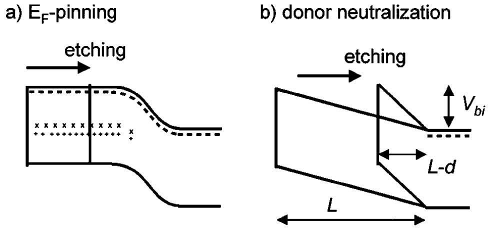

FIG. 2. Schematic band profiles of the near surface regions of reactive-ion etched *n*-GaAs, in which carrier depletion is caused by (a) defect-induced Fermi-level pinning and (b) passivation of dopant impurities.

The slope of the linearly varying part of the data was compared with the Poisson equation for an idealized steplike i/n junction (under the depletion approximation). In this system, the electric field at the surface is given by

$$F(d) = \frac{eN_d}{\varepsilon_s}\left\{\sqrt{(L-d)^2 + \frac{2\varepsilon_s V_{bi}}{eN_d}} - (L-d)\right\} \sim \frac{V_{bi}}{L-d} \tag{2}$$

where N_d is the donor concentration in the n side. The slope is proportional to the inverse of the built-in potential (band bending) V_{bi}.

The solid lines in Fig. 3 were actually obtained by numerically integrating the Poisson equation [13,14], assuming $V_{\mathrm{bi}} = 0.7$ V. The calculation fits well the experimental data in the region 50–190 nm (40–150 nm) for $\mathrm{CHF_3/O_2}$ ($\mathrm{SF_6}$). Thus it is concluded that the *i* layer is nearly intrinsic in these regions. From a further numerical simulation [14], we find that a sizable deviation from the straight-line relationship must have been observed if the residual donor concentration in the *i* layer were larger than $\sim 3 \times 10^{15}$ cm^{-3}. It becomes thus clear that a use of a simple Eq. (1) leads to very large errors invalidating any microscopic analysis. Even in the system where no active donors are present within the *i* layer, the potential drop across it gives a nonzero concentration value. In the meantime, the data for $d < 50$ nm strongly deviates from the straight line in Fig. 3, approaching much smaller field values. We attribute this deviation to the presence of deep levels, which must be induced by the bombardment, causing a Fermi-level pinning near the damaged surface.

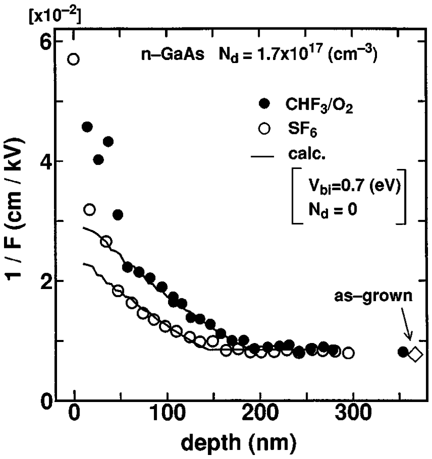

FIG. 3. Reciprocal field determined from the photoreflectance measurements as a function of etched depth. The solid and open circles indicate the data for $\mathrm{CHF_3/O_2}$ and $\mathrm{SF_6}$ RIE, respectively. The data before the RIE is also shown by the diamond (here, the horizontal scale has no meaning). The solid lines were obtained by numerically integrating the Poisson equation for the steplike i/n junction, in which the *i* layer was assumed to be intrinsic ($N_d = 0$) due to the passivation effect, whereas N_d in the n side was taken to be the original donor concentration (1.7×10^{17} cm^{-3}).

The results clearly show the two different deactivation mechanisms occurring after the RIE. The subsurface region is compensated by the damage-induced defects, while the deeper layer is a passivated region. Such information can be hardly obtained from the conventional C-V method. We also point out that the observed critical depth of ~50 nm is consistent with our recent result based on the optically detected magnetic resonance (ODMR): The RIE was found to cause both a passivation of residual defects and defect introduction in the relevant depth range from the surface (25–75 nm) [15].

The observed passivation process must be caused by some fast diffuser. Hydrogen is well known to act this way. In GaAs, both shallow donors and acceptors are efficiently passivated by hydrogen atoms [6]. Annealing study at 450 °C revealed that the original carrier concentration with a uniform profile was restored, both from capacitance and PR methods. This temperature is slightly higher than the recovery stage of hydrogen-passivated shallow impurities in GaAs, 300–350 °C [6]. However, it should be noted here that use of a nominally hydrogen-free RIE gas $\mathrm{SF_6}$ gave almost the same result as that for the $\mathrm{CHF_3/O_2}$ case. Therefore we suggest that the damaged surface area should be very reactive, and this layer may act as a kind of sponge (getter) for residual hydrogen in the chamber. If so, hydrogen should be found within the bulk of wafer after RIE, at the concentration comparable or even exceeding the doping level.

We thus performed a SIMS analysis. The results shown in Fig. 4 confirm the above hypothesis. Hydrogen was indeed detected after the RIE treatments, to a depth exceeding 200 nm from the surface. (A possible role of fluorine on the dopant passivation was excluded since its presence was detected only at the surface.) It should be noted that the introduction depth of hydrogen was almost similar regardless of whether the RIE gas nominally contains hydrogen ($\mathrm{CHF_3}$) or not ($\mathrm{SF_6}$). It is thus likely that the source of the unintentional hydrogenation is not only the etchant gas itself but also other elements of the processing equipment (e.g., water vapor adsorbed on the chamber walls). In the region shallower than 50 nm, where the main cause of the carrier depletion is the Fermi-level pinning, hydrogen was also found at high concentration. Here, the damage-induced point defects may have also formed pair defects with hydrogen atoms

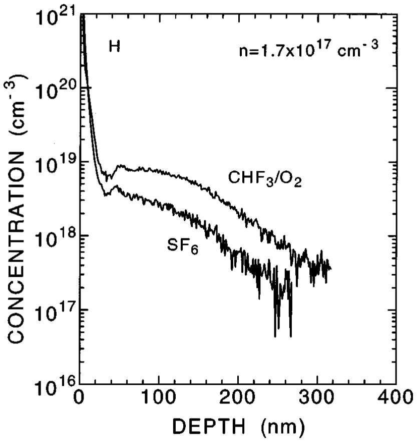

FIG. 4. SIMIS profiles of hydrogen in the RIE samples.

but some of them seem to remain electrically active to cause the Fermi-level pinning. This might result from their multivalent electronic structures. Such centers were detected in our ODMR study of RIE-processed GaAs [15].

In conclusion, the PR spectroscopy combined with the step-etching technique revealed the contribution of two sources for the RIE-induced carrier depletion in GaAs. One is the hydrogen passivation of dopant impurities, which is dominant in the depth region of 50–200 nm. A similar magnitude of this effect was observed for both hydrogen-containing and -noncontaining RIE gas species indicating an extremely efficient gettering activity (sponge-like) of the physically damaged layer. In this shallower region, dopant impurities are mainly compensated and the Fermi level is pinned. The passivation (hydrogenation) is not the dominant mechanism of the carrier depletion there.

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[12] This version of the diagram also holds if doped impurities are compensated by an equal number of shallow centers. However, such a shallow-level compensation scheme must be unstable to the dopant types and concentrations, and thus does not account for the fact that the carrier removal takes place in both *n*- and *p*-type wafers.
[13] A direct integration, instead of analytical calculation, was performed since the etching in the experiment reaches the *n* region. As long as the etched surface stays within the *i* layer, the two calculations give the same results.
[14] The carrier concentration in the deeper-lying *n* region (unmodified region) was taken to be the original value (1.7×10^{17} cm^{-3}).
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