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Formation of highly $n$-doped gallium arsenide layers by rapid thermal oxidation followed by rapid thermal annealing of silicon-capped gallium arsenide

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Carrier concentrations at a level of $\geq 1 \times 10^{19}$ cm$^{-3}$ were achieved when Si-capped GaAs underwent rapid thermal oxidation (RTO) in Ar + 0.1% O$_2$ ambient at 850–1000 °C for 10–60 s followed by rapid thermal annealing (RTA) in Ar ambient at 850–950 °C. Carrier concentrations in the RTO only samples were in the range of $2-5 \times 10^{18}$ cm$^{-3}$. Kinetic data on the diffusion of Si under RTO and RTO + RTA conditions are presented. The enhancement in the electrical activation of the diffused Si during RTA appears to be partly due to its local atomic rearrangement and partly due to redistribution in the GaAs. Ohmic contacts to the doped layer were made using Au–Ga–Ni alloy and contact resistances of $\leq 0.1$ Ω mm were obtained.

Carrier concentrations in Si-doped GaAs even under best molecular beam epitaxy (MBE) growth conditions are limited to $\leq 1 \times 10^{19}$ cm$^{-3}$. Typical $n$ carrier concentrations in Si-implanted/annealed GaAs are limited to $\leq 5 \times 10^{18}$ cm$^{-3}$. It was reported recently that carrier concentrations of $2-5 \times 10^{18}$ cm$^{-3}$ can also be achieved by rapid thermal oxidation (RTO) of Si-capped GaAs. Similar carrier concentrations in GaAs were also achieved by earlier workers using either a heavily doped (a few percent As or P) Si cap or a bilayer of undoped Si and SiO$_2$. In this letter it is demonstrated that carrier concentrations in the Si capped/RTO GaAs can be further enhanced to levels exceeding $1 \times 10^{19}$ cm$^{-3}$ by subsequently rapid thermal annealing (RTA) the Si-capped/RTO GaAs samples at temperatures of $\geq 850$ °C.

Silicon layers of 500 Å were sputter deposited at $10^{-3}$ Torr pressure of Ar on semi-insulating LEC GaAs substrates. Experimental details of RTO of the Si-capped GaAs and Si removal after the RTO have been described previously. In the present investigation the RTO was performed at 850 1000 °C in Ar ambient mixed with 0.1% of oxygen. The oxidized samples were subsequently rapidly thermally annealed at 800–950 °C in Ar ambient with the Si face down. Cross-sectional transmission electron microscopy (XTEM) of the samples after RTO up to 1050 °C showed a nearly smooth Si/GaAs interface. The as-deposited Si was amorphous but it showed epitaxial realignment in the interfacial region after the RTO. After the cap removal, sparsely distributed Si residues were present on the surface of the oxidized GaAs sample.

The distribution of the diffused $^{28}$Si in the GaAs was obtained by secondary-ion mass spectrometry (SIMS) using a 10 keV Cs$^+$ primary beam. Special care was taken to avoid the Si residues in the analysis area during the SIMS analysis. Carrier concentration/sheet resistance-depth distributions were also obtained from a selected number of samples that underwent RTO and RTO + RTA. The GaAs layers were removed sequentially in a controlled manner with an etch rate of 2 Å/s in a solution of 375 H$_2$O:1 H$_2$O$_2$:1 H$_2$SO$_4$ (by volume). Van der Pauw/Hall measurements were performed after the removal of each layer to obtain the sheet resistance/carriers profiles. In-Sn (10%) alloy was used to make ohmic contacts for the measurements. For contact resistance studies, the contacts (width = 25 μm) were fabricated by evaporating Au, Ge, and Ni layers in an e-beam evaporator at $10^{-7}$ Torr pressure followed by an alloying treatment at 470 °C for nominally 0 min. The transmission line measurement (TLM) method was used to determine the contact resistance on the Si-diffused GaAs. The distance between the contacts varied from 4 to 32 μm.

The diffusion of Si into GaAs from a Si cap during RTO has been discussed earlier. Figure 1 shows the diffused Si dose (solid lines) and corresponding sheet carrier density (dashed lines) as a function of RTO temperature. For clarity of presentation data from RTO runs performed for only 10 and 60 s are included in Fig. 1. The data from the other RTO runs of 20 and 120 s although not included also showed similar temperature dependence as that in Fig. 1.

The activation energy of the Si diffusion in GaAs was determined to be 3.5 eV from Fig. 1. This value is higher (by 1 eV) than that reported by Grenier and Gibbons but is in general agreement with that reported by Kavanagh et al. for Si caps doped with 4% P. Based on the sheet carrier concentration data of Fig. 1 and diffusion depths of the Si (SIMS, not shown) from the corresponding samples carrier densities of $2-5 \times 10^{18}$ cm$^{-3}$ are found to be present in the Si-diffused region of the GaAs.

A remarkable increase of $\approx 3$ in the electrical activation of the Si-diffused layer occurred when the RTO of the Si capped GaAs samples was followed by RTA in inert ambient with the original Si cap. For example, the sheet resistance of the sample that underwent RTO at 850 °C for 60 s dropped from 184 to 51 Ω/□ when the RTO was immediately followed by RTA at 850 °C/30 s. Figure 2 shows the carrier concentration-depth profiles corresponding to these samples. Highly doped surface regions with a relatively flat depth distribution (compared to ion implantation) were obtained after the RTO as well as RTO + RTA. The carrier concentration in the RTO + RTA sample exceeded the level of $1 \times 10^{19}$ cm$^{-3}$. Such levels of carrier...
concentration in Si-doped GaAs have previously been achieved only in some of the best MBE-grown material. Figure 2 also includes SIMS profiles of the Si in the RTO only and RTO + RTA samples. A redistribution of the diffused Si apparently occurs during the RTA. It appears that the Si dose \(3.9 \times 10^{14} \text{ cm}^{-2}\) in the RTO + RTA sample was slightly higher than that in the RTO only sample \(3.0 \times 10^{14} \text{ cm}^{-2}\).

A limited number of RTO runs were also conducted with \(^{18}\text{O}\) isotope in the Ar ambient to trace the oxygen diffusion into the Si cap and/or GaAs with a high SIMS detection efficiency. The SIMS analysis of the GaAs after the cap removal did not reveal any diffusion of the \(^{18}\text{O}\) into the GaAs. The diffusion and redistribution of the Si during the RTO and RTO + RTA, respectively, are therefore not related to the presence of oxygen in the GaAs.

Further data on the diffused Si dose as a function RTO time and combined RTO + RTA time at 850 °C are plotted in Fig. 3. In the case of RTO + RTA only RTA time was varied. Also included in the figure are the sheet carrier concentrations corresponding to the two types of samples. It is clear that the dose of the diffused Si increases sharply \((\gtrsim 6)\) from \(3.0 \times 10^{14}\) to \(1.8 \times 10^{15} \text{ cm}^{-2}\) when the RTO time is increased from 60 to 180 s. By comparison the sample with 180 s of combined RTO(60 s) + RTA(120 s) show only a marginal increase \((3.9 \times 10^{14} \text{ cm}^{-2})\) in the diffused Si dose that was already present after the RTO. Yet, the sheet carrier concentrations in the RTO + RTA samples were higher by \(\gtrsim 2\) compared to the RTO only samples. The biggest jump in the carrier enhancement in the RTO + RTA samples occurs during RTA for \(\leq 30\) s, i.e., under conditions where the additional Si diffusion is minimal. The carrier enhancement begins to saturate for longer duration RTAs and eventually deteriorates for annealing times of \(\gtrsim 5\) min. This was further confirmed by the electrical results of the sample \(188 \Omega/\square, 2.6 \times 10^{13} \text{ cm}^{-2}\) which instead of RTO underwent furnace oxidation for 20 min at 835 °C in \(\text{AsH}_3 + 0.1\% \text{O}_2\) ambient. The subsequent RTA at 850 °C/60 s did not show any improvement in the carrier concentration of this sample.

The initial diffusion of Si into the GaAs during RTO is believed to occur when Si self-interstitials are generated by the oxidation at the Si surface. The carrier enhancement during the RTA is related to the following events occurring in the GaAs (ignoring the changes taking place in the Si cap): (i) redistribution of the diffused Si already present after the RTO, (ii) additional Si diffusion from the Si cap,
and (iii) local atomic rearrangement of the diffused Si. In order to better understand the contribution of each of these processes to the carrier enhancement the original Si cap was removed from a limited number of samples after RTA and subsequent RTA was performed under capless condition. The SIMS/electrical data before and after capped/capless RTA in the temperature range of 825-1000 °C are listed in Table I. The symbols $N_s$, $N_S$, $R$, and $\mu$ in the table represent the diffused Si dose from SIMS, sheet carrier, sheet resistance, and Hall mobility, respectively. Comparison of the $N_s$ and $N_S$ values under a variety of RTO conditions shows that $\geq 2$ enhancement in the sheet carrier concentration can occur after capless RTA. There is no additional Si diffusion into the GaAs because the Si cap which acts as a reservoir of the Si diffusion is absent during the capless RTA. It also appears from the table that the higher the initial RTO temperature, the higher the subsequent capless RTA temperature required to achieve $\geq 2 \times 2$ carrier enhancement. The SIMS profiles (not included) show no measurable redistribution of the diffused Si after capless annealing. The enhancement in carrier density is $\geq 3$ when the RTA is performed with the original Si cap. Table I again shows that a small amount of additional Si diffuses into the GaAs during the Si-capped RTA. It is interesting to note that the highest carrier enhancement ($\geq 3$) after RTA occurred in the sample where the depth of the diffused Si was extremely shallow ($\leq 0.1 \mu m$) after RTO (at 825 °C).

The RTA was also performed in capless arsine ambient or with a Si$_2$N$_4$ cap (500 Å) at 900 °C/12 s or 850 °C/60 s, respectively on a selected number of samples after removing the original Si cap. The sheet carrier concentration of these samples again increased by $\geq 2 \times 2$ and no measurable redistribution of the diffused Si occurred. There was no additional diffusion of Si during the latter annealings. There results clearly indicate that the local rearrangement of the already diffused Si alone during a post-RTG heat treatment can account for $\geq 2$-thirds of the total enhancement typically observed during the RTA. The remainder of the enhancement during Si-capped RTA is apparently related to the redistribution of the existing Si and/or additional Si diffusion from the cap. It should be pointed out that in a control experiment where Si-capped GaAs undergoes only RTA (without any RTO) the peak concentration of the diffused Si is approximately $3 \times 10^{17} \text{cm}^{-3}$ at 850 °C/60 s. The level of the additional Si diffusing during RTA (with a Si cap) into the samples which had already undergone RTO is an order of magnitude higher than that in the RTA only samples. This may be related to changes in the doping level as well as the structure of the Si cap after RTO. The cap indeed becomes heavily doped with Ga and As during RTA at levels of $\geq 1 \times 10^{19} \text{cm}^{-3}$ due to the outdiffusion of Ga and As.

Finally, the electrical quality of the ohmic contacts formed on the GaAs doped by the RTO method was determined by TLM measurements. A comparison of contact resistance was made among the following: (i) a control sample which was implanted with Si (30 keV, $4.5 \times 10^{13}$ cm$^{-2}$) and subsequently Si$_2$N$_4$-capped annealed at 810 °C/10 min, (ii) a Si-capped GaAs sample with RTO only at 850 °C/60 s, and (iii) a Si-capped GaAs with RTG at 850 °C/60 s and RTA at 850 °C/30 s. The Si depth distribution in sample (i) was comparable to that in sample (ii). The contact resistance values of 0.16, 0.02, and 0.05 Ω mm, respectively, were obtained from these samples. The latter two values are equivalent because contact resistance values below 0.1 Ω mm cannot be measured accurately by the TLM method. The data clearly demonstrates, that the doped layers formed by the RTO alone or by RTO + RTA can provide extremely low-resistance contacts for GaAs devices.

The authors are grateful to Joe Degelormo for Si cap deposition and arsine annealing, and Marc Albert for part of the RTO/RTA work. Critical comments of Harry Hovel on the manuscript are appreciated.

### Table I. Electrical/SIMS data from the RTO samples before and after RTA with/without (capless) the original Si cap.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>RTA (°C)</th>
<th>$N_s$ (cm$^{-2})$</th>
<th>$N_S$ (cm$^{-2})$</th>
<th>$R$ (Ω cm)</th>
<th>$\mu$ (cm$^2$/V s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>825/60</td>
<td>825/60</td>
<td>$6.4 \times 10^{15}$</td>
<td>$5.5 \times 10^{13}$</td>
<td>$7.7 \times 10^{12}$</td>
<td>$710$</td>
</tr>
<tr>
<td>900/60</td>
<td>800/10</td>
<td>$2.4 \times 10^{14}$</td>
<td>$2.1 \times 10^{14}$</td>
<td>$2.1 \times 10^{14}$</td>
<td>$49$</td>
</tr>
<tr>
<td>925/20</td>
<td>900/10</td>
<td>$2.6 \times 10^{13}$</td>
<td>$1.1 \times 10^{14}$</td>
<td>$6.4 \times 10^{11}$</td>
<td>$56$</td>
</tr>
<tr>
<td>1000/10</td>
<td>950/5</td>
<td>$8.1 \times 10^{12}$</td>
<td>$2.4 \times 10^{15}$</td>
<td>$2.4 \times 10^{14}$</td>
<td>$37$</td>
</tr>
<tr>
<td>1000/60</td>
<td>950/5</td>
<td>$3.3 \times 10^{14}$</td>
<td>$3.3 \times 10^{14}$</td>
<td>$66$</td>
<td>$743$</td>
</tr>
</tbody>
</table>

NM—not measured.

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