Studies on Activation of High-Mobility III-V Group Semiconductor Materials by Using Microwave Annealing

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Abstract: As semiconductors devices scale down, silicon transistors would reach its limitation below 10 nm. Researching for the novel materials, which could replace silicon, is important. In this study, the new potential materials III-V Group compound semiconductors which are ion implanted with low energy and low dose. In order to keep the ultra-shallow junction and get the best activation, the new annealing technology ─ microwave annealing (MWA) is employed. Microwave annealing is a processing with low energy and longer period. In contrast to the conventional high thermal annealing methods such as rapid thermal annealing (RTA), it is a process with high temperature and ultra-short time. However, the high temperature could cause the dopants diffusion and the ultra-short time might make the destroyed lattices repaired not completely. Ion implant with silicon at different temperature (80°C, and 150°C) into In$_{0.47}$Ga$_{0.53}$As(300 nm)/InP substrate, and annealed by low-energy MWA and traditional RTA, respectively to research SPER and electrical activation. By using Raman spectrum, we discover that using MWA energy 2.5P(1.5kW) for 100 s could make the III-V materials achieve SPER by repairing fully. From TEM images, the amorphous layer caused by ion implantation could be recovered to crystal lattices during implantation temperature at 150°C. After annealing by MWA 2.5P(1.5kW) for 100 s, the defects of stacking faults are repaired completely to attain SPER, and it can correspond the Raman results. By using SIMS analysis, it can demonstrate that MWA has better ability to control dopants diffusion. Finally, by using Photoluminescence spectroscopy analysis, the MWA energy 3P(1.8kW) for 100 s could just make silicon dopants get activation. After annealing by MWA 3.5P(2.1kW) for 100 s of implantation at 150°C has the best activation that it has the highest peak.

Keywords: III-V Group, Microwave Annealing, Activation

1. Introduction

III-V group semiconductors have very high electron mobility. The mobility of InSb is higher up to 77000 cm$^2$/Vs, which is more than 48 times of mobility (1600 cm$^2$/Vs) on silicon. III-V group might replace channel material on silicon transistor to improve electron mobility. However, the unknown characteristic on new material would result more techniques that are complex and requiring more precise semiconductor process. For III-V compound semiconductors, we can dope the material to be n-type by incorporating a group VI elements into a group V of III-V because group VI has one electron more than group V. And we can dope the material to be p-type by incorporating a group II elements into a group III of III-V because group II has one electron less than group III. For example, doping group VI such as sulfur into InP would be n type. If we dope the material of group IV elements, it would have two situations: 1. Doping a group IV elements into a group V would be p-type because group IV has one electron less than group V. 2. Doping a group IV elements into a group III would be n-type because group IV has one electron more than group III. Thus doping group IV into group III-V materials is interesting. And doping group III or V materials into III-V compound semiconductors is ineffective.

Group IV as amphoteric dopants can behave as either donors or acceptors depending on the lattice they occupy. In practice, they tend to prefer either the group III or group V site to create n or p type regions. The most common n-type
amphoteric dopant used in group III-V such as InGaAs, and InP is Silicon. Silicon remains the most attractive n-type dopants in InGaAs due to its limited diffusivity and post implant activation values of 0.9-1×10^{19}/cm^2. Generally the activation of Si improves with increasing annealing temperature however Si has been shown to change types in GaAs where it goes from n to p type at annealing temperatures above 1050°C [1, 2, 3].

2. Experimental Scheme

The experimental flow of the III-V group is shown as figure 1. Commercially available (100) n-type S-doped InP wafers with 300nm lattice-matched In_{0.63}Ga_{0.37}As of epitaxial by MOCVD were used in this paper. All wafers were ion implanted with tilting 7° by silicon ions at 20keV, @6E14 atoms/cm^2 at 80 and 150°C. According to Kevin S. Jones group research, it demonstrated that elevating implantation temperature could help destroyed lattices with recovery to avoid amorphous layers [4, 5, 9]. Prior to annealing, 15nm protective layer Al_{2}O_{3} was deposited by ALD to prevent surface degradation, and the previous literature has proved that using Al_{2}O_{3} for capping layer could prevent surface degradation due to group V easily loss [6, 7]. After capping Al_{2}O_{3} on In_{0.63}Ga_{0.37}As, they were annealed by MWA 1P(0.6kW)–4P(2.4kW) for 100 s and by RTA 450–750°C for 8 s, respectively. Next, 49% buffered hydrofluoric acid (HF) solution was used to etch Al_{2}O_{3} before the characterization analysis. Finally, the structural characterization was performed with cross-sectional TEM after ion implantation and after annealing to compare the as implanted microstructures with those of the post annealing SPER microstructures. The internal characterization of annealed specimens was measured by using optical spectrum of Raman spectrum and Photoluminescence spectroscopy (PL). Secondary ion mass spectrometry (SIMS) was performed on the annealed samples to determine the Si distribution profiles. Electrical characterization was performed with Hall effect and sheet resistance.

3. Results and Discussion

3.1. Effect of Ion Implantation Temperature

The cross-sectional TEM images of Si^{+} (20keV, @6E14) implant into In_{0.63}Ga_{0.37}As at room temperature (RT), 80°C, and 150°C. In the case of implantation at room temperature(RT), an amorphous layer(a-layer) extending about 35 nm from the surface of the specimen as shown in figure 2(a). It is known that avoiding amorphization by increasing the implantation temperature results in higher dopant activation in III-V compound semiconductors [8].

In the case of implantation at 80°C, an amorphous layer(a-layer) remaining about 26 nm from the surface as shown in figure 2(b). It has demonstrated that the implantation temperature of 80°C can assist in recovering amorphization. TEM image of figure 2(c) does not reveal the presence of an a-In_{0.47}Ga_{0.53}As layer. Thus, the implantation temperature of 150°C is sufficient to prevent an amorphous layer during the implantation. The effect of high-implantation temperature of 150°C is to recrystallize the amorphized In_{0.47}Ga_{0.53}As effectively. For implantation temperatures of 150°C, amorphization is avoided but damage to the crystal lattice decreases with increasing implantation temperature.

![Figure 2. TEM images of Si-implanted In_{0.47}Ga_{0.53}As at implantation temperature of (a)room temperature(RT), (b)80°C, and (c)150°C.](image)

3.2. Micrograph Analysis

The Si-implanted specimens after annealing at RTA as shown in figure 3 (a)-(c), and MWA as shown in figure 3 (d)-(g). In the case of annealed specimen at RTA 450°C for 8 s, the amorphous layer does not exist as shown in figure 3(a). But it exhibits a highly defective regrown layer as evidenced by the presence of stacking faults about 15 nm on the surface on the close pack (111) planes result from SPER of In_{0.47}Ga_{0.53}As [9]. Other literatures have shown that III-V arsenide’s generally exhibit highly defective regrown layers after low temperature annealing treatments [10, 11, 12, 13]. In the case of annealed specimen at RTA 500°C for 8 s, it still exists defective regrown layer but the remaining defects are less as shown in figure 3(b). For the case of annealed specimen at RTA 550°C for 8 s, there is no stacking faults observed from (c). On the other word, the heating level of RTA 550°C can recrystallize the a-In_{0.47}Ga_{0.53}As and repair defects completely.

In the case of annealed specimen at MWA 1P(0.6kW) for 100 s, the amorphous layer is recrystallized but a defective layer of stacking faults about 15 nm apparently as shown in figure 3(d), which situation is like the annealed sample of RTA 450°C. The TEM image of annealed specimen at MWA
1.5P(0.9kW) for 100 s as shown in figure 3(e), high density of stacking faults still exists while a little defect is remaining as shown in figure 3(f) for the case of annealed specimen at MWA 2P(1.2kW) for 100 s. For the case of annealed specimen at MWA 2.5P(1.5kW), no stacking faults is remaining as shown in figure (g), which is like the annealed sample of RTA 550°C. That is to say, the defective layer of stacking faults could be repaired fully to achieve SPER after processing annealing by RTA 550°C for 8 s and MWA 2.5P(1.5kW) for 100 s. It has proved that the annealing condition of MWA can use low-energy of 2.5P(1.5kW) that its actual temperature is lower than 500°C to attain SPER.

3.3. Spectral Analysis

The Raman spectrum was measured at room temperature by using the 532 nm line of an Ar+ laser as excitation source with a charge-coupled device (CCD) detector, and the power was at the 1.3 mW. Figure 4 and 5 show Raman spectrums of Si-implanted In$_{0.53}$Ga$_{0.47}$As at 80°C sample and annealed samples by RTA and MWA separately with increasing temperature and energy. Take previous paper of the result of Raman spectrums of Si-implanted In$_{0.53}$Ga$_{0.47}$As for reference [14]. The spectrum of the as-grown sample (300 nm In$_{0.53}$Ga$_{0.47}$As on InP) is dominated by two main peaks of InAs-like Longitudinal optical (LO) mode at 244 cm$^{-1}$ and GaAs-like LO mode near 270 cm$^{-1}$, and the weak second-order optical modes for GaAs-like 2LO mode near 500 cm$^{-1}$. Si$^+$ (20 keV, @6E14) implantation at 80°C in In$_{0.53}$Ga$_{0.47}$As results in the formation of a fully amorphized and this spectrum marked as the “imp-80” shows no obvious peaks. With raising annealing temperature and energy, the spectrums of the annealed samples at RTA 450°C−500°C and MWA 1P−2P display an obvious GaAs-like LO Raman peak with a noticeable lattice recovery of implanted sample. Which demonstrates from TEM micrograph that no amorphous layer is remaining in annealed samples. With increasing annealing temperature and energy up to RTA 550°C and MWA 2.5P, the Raman spectrum shows a gradual intensity increase and sharpening of optical GaAs-like LO mode. In the spectrum of the annealed samples at RTA 550°C and MWA 2.5P, the GaAs-like LO Raman peaks near 270cm$^{-1}$ display highest. Therefore, we conclude that an excellent lattice recovery is already achieved by RTA 550°C for 8 s and MWA 2.5P for 100 s, separately. With a further increase of annealing temperature and energy, the only noticeable effect on the Raman spectrum of annealed samples at RTA 600°C and MWA 3P is an intensity reduction. Which signals the onset of electrical activation of the implanted impurities [14]. As increasing of the annealing temperature and energy, the spectrums show four Raman peaks to reflect the increasing electrical activation of the implanted dopants mentioned from previous literature [14]. The similar four Raman peaks are observed in the spectrum of MWA 4P and RTA 700°C and 750°C.

Figure 3. TEM images of Si-implanted In$_{0.47}$Ga$_{0.53}$As at implantation temperature of 80°C and post annealing by RTA from 450°C to 550°C for 8 s [(a)-(c)] and MWA from 1P(0.6kW) to 2.5P(1.5kW) for 100 s [(d)-(g)].

Figure 4. Raman spectrums of implanted at 80°C and be annealed by RTA.

Figure 5. Raman spectrums of implanted at 80°C and be annealed by MWA.

The similar results is observed from the Raman spectrum of Si-implanted In$_{0.53}$Ga$_{0.47}$As at 150°C sample and annealed samples by RTA and MWA as shown in figure 6 and 7. However, the spectrum of Si-implanted In$_{0.53}$Ga$_{0.47}$As at 150°C sample displays more obvious GaAs-like LO peak near 270cm$^{-1}$ than “imp-80”. The Raman results could verify the TEM images that implantation temperature of 150°C sample could recrystallize the amorphous layer because the Raman peak of imp-150 is higher than imp-80. With increasing annealing temperature and energy on implanted samples at 150°C, the similar situation of the intense and sharpening GaAs-like LO peaks are seen in the spectrum of annealed samples at RTA 550°C and MWA 2.5P. It could
correspond the TEM micrograph of low-energy MWA at 2.5P(1.5kW) displaying no defects because it indicates excellent lattice recovery to achieve SPER. When the peak intensity of the GaAs-like LO reduces as shown in the spectrum of annealed samples at RTA 600°C and MWA 3P, it indicates the beginning to activate dopants electrically.

![Figure 6. Raman spectrums of implanted at 150°C and be annealed by RTA.](image)

![Figure 7. Raman spectrums of implanted at 150°C and be annealed by MWA.](image)

The room-temperature PL spectroscopy was performed by using 1064 nm pulsed fiber laser with an InGaAs detector, and the peak power was set at 3 kW. The PL results for the bulk of 300 nm In_{0.53}Ga_{0.47}As epitaxy on InP and the Si-implanted at 80°C and post annealed by RTA and MWA samples are as shown in figure 8 and 9, separately. The spectrum of the bulk of the virgin In_{0.53}Ga_{0.47}As shows the main two peaks near 1450 and 1600 nm. However, the energy bandgap of In_{0.53}Ga_{0.47}As is 0.75 eV, and the correspondent wavelength is 1653 nm. The actual PL measurement is different from the physical theory in materials because the actual growth situation of In_{0.53}Ga_{0.47}As epitaxy on InP would cause the different PL spectrum. We could take the spectrum of “rychle rostlý InGaAs” as a reference because it shows similar peaks to our PL result of the bulk. [12]

![Figure 8. PL spectrum of the bulk, and the implanted sample at 80°C after annealing by RTA.](image)

![Figure 9. PL spectrum of the bulk, and the implanted sample at 80°C after annealing by MWA.](image)

Figure 10 displays the small signals which are combined from the PL spectrum of the implanted sample at 150°C and post annealed by RTA and MWA. In the case of annealed specimens at RTA 550°C and MWA 2.5P, the main peak of PL spectrums near 1600 nm is intense, which is similar to the situation of implanted sample at 80°C. The signal of annealed specimens at MWA 2.5P is even more intense than at RTA 550°C. It demonstrates that the specimen of implanted at 150°C and post annealed at MWA 2.5P has better recovering amorphization ability than at RTA 550°C.

![Figure 10. Combine the small PL signals from the implanted-150°C samples after annealing by RTA and MWA.](image)
Figure 11 displays the strong signals which are combined from the PL spectrum of the implanted sample at 150°C and post annealed by RTA and MWA. The signals of annealed specimens at RTA 600°C and MWA 3P show higher obviously than small signals because the electrical activation is already achieved. In the case of annealed sample at MWA 3.5P, the most intense two peaks than other annealed samples by MWA are shown, it indicates the best activation electrically. High implantation temperature of 150°C could result in higher dopant activation because of no amorphous layer remaining after implantation, so the annealing level would require lower energy than in implanted samples at 80°C.

The de-activation reaction might have taken place at annealed by RTA 700°C and MWA 4P because the two peaks of them are lower than the PL signal of annealed at MWA 3.5P. The highest signal is shown in the spectrum of annealed sample at RTA 750°C, and it indicates good activation but the high temperature would cause dopant diffusion.

3.4. SIMS Analysis

Figure 12 shows the SIMS results of Si-implanted at 80°C and post annealed by different energies MWA at 2.5P(1.5kW)–4P(2.4kW). The silicon profiles of those are nearly indistinguishable, and it indicates almost no diffusion. It clarifies that the heating method of MWA could not cause dopant diffusion. That is to say, the SIMS results demonstrates that the annealing method of MWA is better to control diffusion profiles than RTA. And SIMS results has proved that the guess that the annealing condition of RTA 750°C might result in diffusion from PL spectrum results.

4. Conclusion

TEM images, the implantation temperature of 150°C can regrow the amorphous layer effectively resulting in higher dopant activation in following annealing. The annealing condition of MWA 2.5P and RTA 550°C can repair the high-density defects of stacking faults completely to accomplish SPER. The Raman spectrums show the highest main peak on the annealing condition of MWA 2.5P(1.5kW) and RTA 550°C. It demonstrates that MWA 2.5P can use lower energy which actual temperature is about 450°C than RTA 550°C to achieve SPER. As the annealing energy increases, the main peaks reduce because it begins to activate the dopant electrically. The Raman spectrum results can correspond the TEM results that the annealing conditions of MWA 2.5P(1.5kW) and RTA 550°C have the highest peaks. High PL signals could correspond the sheet resistance low, and it represents that the activation level. The PL signals of MWA 2.5P and RTA 550°C has the highest peak from small signals, and it corresponds the Raman that they achieve SPER. And the PL spectrum of MWA 3P and RTA 600°C has strong signals that they start to activate dopants electrically. The PL signals of annealed samples at implantation temperature of 150°C are stronger than at implantation temperature of 80°C because the implantation temperature of 150°C can repair the amorphous layer resulting in higher dopant activation after annealing. And the best activation of the highest PL signal is located on the annealing condition of MWA 3.5P of implantation temperature at 150°C. It proves that MWA could use lower energy than RTA to achieve dopant activation effectively. From SIMS profiles of annealed samples by RTA and MWA, higher temperature of RTA 600°C causes silicon distribution deeper slightly while the silicon profiles of MWA are almost the same. It demonstrates that MWA has better ability to control dopant diffusion than RTA.

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