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Effects of point defect healing on phosphorus implanted germanium n^+/p junction and its thermal stability

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In this work, the effect of Ge point defect healing process between 550 °C and 650 °C is investigated, in the aspect of leakage (off) current and junction depth of Ge n^+/p junction diodes using ECV, TEM, J-V, and SIMS analyses. After 600 °C anneal, off-current density (2×10^{-4} A/cm²) is dramatically reduced due to the defect healing phenomenon that decreases the number of point defects, subsequently providing a higher on/off-current ratio of 5×10^3 . In spite of the high healing temperature, junction diodes seem not to suffer from the deep diffusion of phosphorus (P) in Ge because those diffuse mostly through V_{Ge} . In addition, it is also confirmed that Ti is an appropriate material in terms of diffusion barrier and diffusivity for Ge n^+/p junction contact metal. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4820580>]

I. INTRODUCTION

Germanium (Ge) is one of the attractive candidates for next generation complementary metal oxide semiconductor (CMOS) due to its higher carrier mobility¹ and lower processing temperature^{2,3} compared to silicon (Si). However, conventional ion implantation process for source/drain (S/D) junction formation causes severe crystal damage and it consequently increases the number of point defects consisting of Ge vacancy (V_{Ge}) and self-interstitial (Ge_i) atoms.⁴ Since these point defects work as recombination trap centers in Ge, it induces generation current (I_G) and thereby increases the total junction leakage current. In addition, fast diffusion of n-type dopants through V_{Ge} is hinders shallow S/D junction fabrication.⁵⁻⁷ Although rapid thermal annealing (RTA),^{8,9} laser annealing (LA),^{10,11} metal induced dopant activation (MIDA)^{12,13} techniques have been developed to achieve shallow and high quality junction interface in Ge, the obtained S/D junctions are still not free from the leakage and fast diffusion problems due to unhealed point defects. Recently, several research groups have proposed hydrogen and fluorine-based passivation methods^{14,15} to reduce the number of V_{Ge} , and we also have reported the healing phenomenon of point defects in Ge by high temperature and long annealing process.¹⁶ These studies confirm Ge point defects reduction through transmission electron microscopy (TEM), deep level transient spectroscopy (DLTS), or spreading resistance profiling (SRP) analysis. In this paper, the healing phenomenon of Ge point defects is not only confirmed by the high temperature—long anneal process but its

effect on leakage (off) current and junction depth in Ge n^+/p junction diodes is also investigated through electrochemical capacitance-voltage (ECV), transmission electron microscopy (TEM), current density-voltage (J-V), and secondary ion mass spectroscopy (SIMS) analyses. In addition, the electrical degradation of optimally healed Ge n^+/p junction diodes with Ni or Ti contact is analyzed according to post-fabrication process temperatures between 250 °C and 350 °C.

II. EXPERIMENTAL

About 2.6 μm thick high quality crystalline intrinsic Ge (p-type: $\sim 5 \times 10^{14} \text{ cm}^{-3}$) layer was grown heteroepitaxially on a p-type Si substrate using multistep hydrogen annealing (MHAH) growth method.¹⁷ For the first part of the experiment, 20 nm thick SiO_2 layer was deposited on the Ge layer in a low-pressure chemical vapor deposition (LPCVD) system to avoid surface damage by ion implantation. In order to create intentional Ge point defects (V_{Ge} and Ge_i), Ge ions with dose of $1 \times 10^{14} \text{ cm}^{-2}$ were then implanted into the Ge region at 180 keV. The implanted samples were thermally annealed at 500 °C, 600 °C, and 700 °C for 1 h in N_2 ambient using a thermal furnace and ECV measurement was performed on the samples to confirm the healing phenomenon of V_{Ge} according to annealing temperature. For the second experimental part, 20 nm thick Al_2O_3 layer was deposited on the Ge layer by an atomic layer deposition (ALD) system to prevent surface damage by ion implantation and also to passivate the Ge surface. Phosphorus (P) ions were then implanted into the Ge layer at 60 keV with 10^{15} cm^{-2} dose to achieve n^+ Ge region. The samples were annealed at 550 °C, 600 °C, and 650 °C for 1 h in a N_2 ambient to activate P atoms as well as to heal V_{Ge} , followed by titanium (Ti)/aluminum

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(Al) deposition with a metal shadow mask to form contact electrodes. J-V measurement was finally performed on the fabricated junction diodes together with TEM, SIMS, and ECV analyses to investigate the effect of V_{Ge} healing on leakage current and junction depth of the junction diodes. For the third experimental part to study the thermal stability of the diodes, sample with nickel (Ni) instead of Ti as a contact metal was additionally prepared and was compared with Ti contact junction diodes through J-V and SIMS analyses after performing post-fabrication anneal at 250 °C, 300 °C, and 350 °C for 10 s in a RTA system.

III. RESULTS AND DISCUSSION

Crystal damages induced during ion implantation process are known to form Frenkel pairs consisting of V_{Ge} and Ge_i , as shown in (i) of Fig. 1(a). After going through high temperature annealing process, (ii) the Frenkel pairs are eliminated due to recombination of Ge_i and V_{Ge} and (iii) consequently

point defects are healed. In order to confirm the defect healing phenomenon according to annealing temperature, defects are intentionally generated by implanting Ge ions into the Ge layer. These samples are then annealed at various temperatures (500 °C, 600 °C, and 700 °C). Fig. 1(b) shows the carrier concentrations of the annealed Ge samples, which are estimated by ECV analysis. Because it is difficult to measure the precise carrier concentration near surface region through ECV method, the concentration data were extracted at the 300 nm below surface where the tail region of implanted Ge atoms is located and the carrier concentration is uniformly distributed as a function of depth. In the case of Ge implantation with high energy of 180 keV, the tail is observed even below 1 μ m deep region without additional annealing process. In addition, V_{Ge} and Ge_i are uniformly distributed from surface to bulk regions after the long time annealing process due to the high diffusivity values of Ge_i (1×10^{-5} cm²/s at 600 °C) and V_{Ge} (4.8×10^{-8} cm²/s at 600 °C),¹⁸ consequently making the Frenkel pairs recombination to occur at both surface and bulk regions. Very high p-type concentration was observed in the as-implanted sample due to V_{Ge} with acceptor level at 0.20 eV above the top of the Ge valence band.¹⁹ However, this concentration reduced with higher annealing temperatures owing to the recombination of V_{Ge} and Ge_i . Although there are also Ge_i atoms with donor level at 0.04 eV bottom of the conduction band¹⁹ or 0.15 eV above the top of the valence band,²⁰ the measured carrier concentration is presented as p-type because Ge_i moves deeper from the junction and V_{Ge} with acceptor charge level in the Ge energy band resides near the surface.^{21,22}

As shown in Fig. 2(a), J-V characteristics of the Ge n⁺/p junction diodes annealed at 550 °C, 600 °C, and 650 °C are measured to investigate the effect of point defect healing phenomenon on the off-current. The 550 °C and 650 °C annealing range for Ge n⁺/p junctions were selected because, (1) 500 °C or above anneal is normally needed to activate n-type dopants fully in Ge²³ and (2) effective defect healing phenomenon was observed above 600 °C (Fig. 1). We also note that the J-V characteristics are analyzed through the previously obtained V_{Ge} concentration data because it is hard to estimate accurately the concentration of V_{Ge} created after P implantation by ECV. On/off-current ratio and on-current density were extracted at $|V| = 1$ V in the J-V curves and are plotted in Fig. 2(b) as a function of annealing temperature. Based on the succeeding SIMS data (see Fig. 4(a)), the diffusivity of P atoms was estimated to be 7.09×10^{-16} cm²/s at 550 °C, which was much slower than that of V_{Ge} (4.12×10^{-8} cm²/s).¹⁸ A number of V_{Ge} left near surface region due to preferential momentum transfer²² are also expected to be distributed uniformly from surface to bulk region by its high diffusivity at each annealing temperatures. Since the V_{Ge} which is not healed after annealing at 550 °C acts as a recombination trap center in Ge n⁺/p junction interface, a high generation current (I_G) was observed in the junction sample annealed at 550 °C. Above 600 °C, because the number of V_{Ge} was significantly decreased, the annealed junction sample showed dramatic decrease of off-current density while maintaining on-current density, which subsequently provided a higher on/off-current ratio of 5×10^3 . However, V_{Ge} working as a recombination

FIG. 1. (a) Schematic diagram for the defect healing phenomenon. (b) Carrier concentrations extracted through ECV measurement at 300 nm deep region from surface of the Ge implanted samples non-annealed and annealed at 500 °C, 600 °C, and 700 °C.

FIG. 2. (a) J-V characteristics of the Ge n^+/p junction diodes annealed (or activated) at 550 °C, 600 °C, and 650 °C for 1 h. (b) On/off-current ratio and on-current density of the junction diodes as a function of annealing temperature at $|V| = 1$ V.

trap still seemed to remain in the junction interface, making the off-current to increase as a function of reverse voltage bias. Since the number of V_{Ge} was continuously reduced by the point defect healing process with increased annealing temperature (Fig. 1(b)), it can be expected from the junction sample annealed at 650 °C that (1) most of the point defects are healed, (2) I_G is reduced through the increased carrier lifetime, and (3) off-current density is finally saturated. In addition, because the hole concentration is reduced by the number of V_{Ge} with acceptor charge level, diffusion current (I_{Diff}) which is inversely proportional to the concentration of lightly doped p-type region seems to increase. As a result, when compared to the junction sample annealed at 600 °C, saturated off-current density was obtained due to the reduced I_G in the 650 °C annealed junction, but the total leakage current density was increased through the increase of I_{Diff} . Fig. 3 shows the cross-sectional TEM images of Ge n^+/p junctions; (a) non-annealed and (b) annealed at 600 °C. Although the ion implantation process of n-type dopants (P ions) initially damages the Ge surface region up to 64 nm in depth, this region seems to recrystallize after 600 °C anneal, indicated by the interface between (I) damaged and (II) non-damaged regions shifting towards the Ge surface. Even though the implanted (damaged) region does not seem to have a crystal lattice structure, it is hard to conclude that the region is fully amorphized since the dose of implanted P ions is not sufficient for a full amorphization of the region ($10^{15} cm^{-2}$). In addition, we also note that the TEM images of as-implanted and recrystallized samples

FIG. 3. Cross-sectional TEM images of the Ge n^+/p junctions (a) non-annealed and (b) annealed at 600 °C. Region I and II respectively indicate damaged and non-damaged regions by an ion implantation process.

(at 600 °C) only show the highly damaged regions, where the lowly damaged tail regions are not shown.

Fig. 4(a) shows the chemical concentrations (SIMS profiles) of P atoms in the 600 °C annealed sample as a function of junction depth and their fitted profiles which consist of Gaussian (region I) and Error (region II) functions. The difference of crystal quality at surface and deep junction regions induced by an ion implantation process makes out-diffusivity of P atoms to have slightly different values when compared to in-diffusivity. In the region I showing Gaussian distribution, P atoms were piled up near the surface by the out-diffusion and surface back-scattering phenomena. However, it was also observed that P atoms diffusing toward the bulk region followed an Error function distribution (region II), where the P atoms piled-up in region I served as an infinite source. In order to investigate these two different dopant distributions in more detail, diffusivity and pile-up ratio (piled-up concentration in region I/total concentration) extracted from Gaussian fitted curve in the region I were first plotted as a function of annealing temperature in Fig. 4(b). As the annealing temperature increases, the pile-up ratio increased due to enhanced diffusion phenomenon at higher annealing temperature, indicating that more number of P atoms flowed into the region I. As shown in Fig. 4(c), activation energy (E_A) and pre-exponential factor were also estimated to be respectively 1.09 eV and $3.12 \times 10^{-9} cm^2/s$ in the region II by fitting the distributed P atoms through the least square method. Although similar diffusivity was reported at 600 °C by Chui *et al.* ($4.91 \times 10^{-14} cm^2/s$),⁸ it is predicted that RTA process did not provide enough thermal energy and time to heal V_{Ge} and consequently high pre-exponential factor ($4.38 \times 10^{-2} cm^2/s$) was observed. In addition, Carroll *et al.*⁷ and Koffel *et al.*²⁴ also reported similar high pre-exponential factors ($1.85 \times 10^{-2} cm^2/s$ and $10^{-2} cm^2/s$). It is thought that in these works much more number of V_{Ge}

FIG. 4. (a) SIMS concentration profile of P atoms in 600 °C annealed sample as a function of junction depth and its fitted profiles by Gaussian (region I) and Error (region II) functions. (b) Diffusivity and pile-up ratio (piled-up concentration in region I/total concentration) extracted from Gaussian fitted curve in region I as a function of annealing temperature. (c) Diffusivity and junction depth extracted from Error function fitted curve in region II as a function of annealing temperature.

was created during the implantation process due to its higher energy (160 keV) and dose (10^{16} cm^{-2}), which were not sufficiently healed, and subsequently enhanced the diffusion of P atoms. In this work, because P atoms are able to diffuse mostly through V_{Ge} ,⁵ the defect healing phenomenon by high temperature annealing process prevented the diffusivity of P atoms from being increased as a function of annealing temperature and consequently the junction depth did not increase much in spite of performing high temperature anneal between 550 °C and 650 °C.

As shown in Fig. 5, the concentrations of electrically activated P atoms were measured as a function of junction depth by ECV for samples annealed 550 °C, 600 °C, and

FIG. 5. SIMS and ECV profiles measured in the Ge n^+/p junction diodes non-annealed and annealed at (a) 550 °C, (b) 600 °C, and (c) 650 °C. Blue dashed line indicates the starting measurement point of doping profile confirmed by ECV analysis.

650 °C along with SIMS profiles for comparison. First, as previously discussed, the difference of crystal quality at surface and deep junction regions made two different distributions; (1) Gaussian function in the region I due to the out-diffusion and surface back-scattering phenomena and (2) Error function in the region II because of the piled-up dopants serving as an infinite source for this in-diffusion. Although more number of P atoms is piled up at the surface region (I), it does not mean that the number of the electrically activated P atoms were increased because the starting measurement points of doping profiles confirmed by ECV

analysis were, respectively, 25 nm, 33 nm, and 39 nm at 550 °C, 600 °C, and 650 °C. Since depletion width indicating the starting measurement point is inversely proportional to a carrier concentration, lower electrically activated P concentration is expected at the surface region as the annealing temperature increases. In addition, we also confirmed that ECV profiles are almost coincide with SIMS data at the deep junction region, indicating that most of P atoms at the region II were successfully activated by high thermal energy supplied above 550 °C.

Finally, in order to investigate thermal stability of the healed junction diodes, Ni and Ti were selected as a contact metal for the 600 °C annealed (or healed) junction diode samples. These two diodes were analyzed and compared after going through the post-fabrication anneal at 250 °C, 300 °C, and 350 °C for 10 s. Fig. 6 shows (a) J-V characteristics of the Ge n^+/p junction diodes with Ti contact and (b) on/off-current ratio / on-current density data extracted from the J-V curves. After the 250 °C short time annealing process, off- and on-current densities are decreased due to additional crystallization induced by Ti¹³ and high resistivity of Ti germanide phase formed at 250 °C,²⁵ respectively. As shown in Fig. 8(a), small amount of Ti atoms seems to diffuse into the junction at this temperature because of its relatively low diffusivity in Ge, forming larger grains in the junction interface through small number of heterogeneous nuclei during metal-induced crystallization (MIC),^{13,26} which subsequently reduces I_G . We previously reported a

similar phenomenon in the Ge n^+/p junction diodes activated by cobalt (Co) at 360 °C.¹² However, as RTA temperature increases up to 350 °C, the off-current density was dramatically increased because more number of Ti atoms worked as recombination centers in Ge is placed in the junction interface. The SIMS intensity of Ti in the 350 °C RTA processed sample seems to be increased about 100 times in Fig. 8(a) when compared to the 250 °C sample. In addition, on-current density increased above 300 °C annealing since another Ti germanide phase with relatively low resistivity was achieved at the temperatures.²⁵ Similarly, in Fig. 7 showing (a) J-V characteristics of the Ge n^+/p junction diodes with Ni contact and (b) on/off-current ratio / on-current density data extracted from the J-V curves, it is confirmed that off- and on-current density were respectively decreased and increased after annealing above 300 °C. The increase of on-current density seems to be attributed to Ni germanide formation reducing the contact resistance. However, because of relatively faster diffusion of Ni atoms in Ge compared to Ti,^{12,27} increase of off-current density and decrease of on/off-current ratio are expected even at 250 °C. In fact, the on/off-current ratio continuously reduced as the RTA temperature increased. As shown in Fig. 8(b), degree of Ni diffusion at 250 °C is similar to that of 350 °C, indicating that large amounts of Ni traps are already located in the junction interface even after 250 °C low temperature anneal. Therefore, it

FIG. 6. (a) J-V characteristics of the Ge n^+/p junction diodes with Ti contact, which are non-annealed and annealed at 250 °C, 300 °C, and 350 °C for 10 s. (b) On/off-current ratio and on-current density data extracted from the J-V curves at $|V| = 1$ V.

FIG. 7. (a) J-V characteristics of the Ge n^+/p junction diodes with Ni contact, which are non-annealed and annealed at 250 °C, 300 °C, and 350 °C for 10 s. (b) On/off-current ratio and on-current density data extracted from the J-V curves at $|V| = 1$ V.

FIG. 8. SIMS profiles of (a) Ti and (b) Ni in the Ge n^+/p junction diode samples with Ti or Ni contact, which are annealed at 250 °C and 350 °C for 10 s.

is thought that Ti which can work as diffusion barrier²⁸ and diffuse itself slowly into Ge junction is an appropriate contact metal in most of Ge n^+/p junctions fabricated by this defect healing process as well as the previously mentioned techniques, such as RTA, LA, and MIDA.

IV. CONCLUSION

In this work, we not only confirmed the healing phenomenon of Ge point defects by high temperature—long time anneal but also investigated its effect on off-current and junction depth in Ge n^+/p junction diodes through ECV, TEM, J-V, and SIMS analyses. After annealing above 600 °C, a dramatic decrease in off-current density was observed, maintaining on-current density and subsequently providing a higher on/off-current ratio of 5×10^3 , because the number of V_{Ge} significantly decreased by defect healing. In spite of the high temperature anneal between 550 °C and 650 °C, the junction diodes seemed not to suffer from deep diffusion problem because P atoms diffuse mostly through V_{Ge} .⁵ In addition, electrical degradation of optimally healed Ge n^+/p junction diodes with Ni or Ti contact according to post-fabrication process temperature between 250 °C and 350 °C was analyzed. The relatively fast diffusion of Ni atoms in Ge when compared to Ti^{12,27} increased the off-current

density and also decreased on/off-current ratio at 250 °C, and this on/off-current ratio continuously reduced with increasing RTA temperature. As a result, it was confirmed that Ti is the appropriate material in terms of diffusion barrier and diffusivity for contact metal for Ge n^+/p junctions.

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