Strain conservation in implantation-doped GeSi layers on Si(100)

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ABSTRACT

Metastable pseudomorphic GeSi layers grown by vapor phase epitaxy on Si(100) substrates were implanted at room temperature. The implantations were performed with 90 keV As ions to a dose of $1x10^{13}$ cm^{-2} for $Ge_{0.08}Si_{0.92}$ layers and 70 keV BF_2^+ ions to a dose of $3x10^{13}$ cm^{-2} for $Ge_{0.06}Si_{0.94}$ layers. The samples were subsequently annealed for short 10-40 s durations in a lamp furnace with a nitrogen ambient, or for a long 30 min period in a vacuum tube furnace. For $Ge_{0.08}Si_{0.92}$ samples annealed for a 30 min-long duration at 700 °C, the dopant activation can only reach 50% without introducing significant strain relaxation, whereas samples annealed for short 40 s periods (at 850 °C) can achieve more than 90% activation without a loss of strain. For $Ge_{0.06}Si_{0.94}$ samples annealed for either 40 s or 30 min at 800 °C, full electrical activation of the boron is exhibited in the GeSi epilayer without losing their strain. However, when annealed at 900 °C, the strain in both implanted and unimplanted layers is partly relaxed after 30 min, whereas it is not visibly relaxed after 40 s.

INTRODUCTION

Pseudomorphic Si/GeSi heterostructures have been extensively studied in terms of crystal growth, characterization of structural and physical properties, and device applications [1-4]. The doping of strained GeSi layers has been performed mainly by in-situ methods during the growth of a film. The main advantage of these methods over ion implantation is that doping is possible with minimal effects on the strain of the layers. One drawback of these methods is that they are limited to laterally uniform doping profiles. N-type doping of strained GeSi layers by phosphorous implantation has been successfully performed and demonstrated by Lie et al. without losing strain in the GeSi layer when the dose of implantation is low, i.e. no amorphized layer is formed [5]. According to Lie et al., amorphization caused by high-dose implantation always leads to the strain relaxation in GeSi layers as they regrow[6,7]. For p-type doping by implantation, only a few studies of B^+ or BF_2^+ implantation have been reported [8,9]. However, those studies don't include the electrical behavior of implanted dopants in GeSi even though an anomaouls electrical behavior of p-type doped strained GeSi was reported before [10,11]. In this paper, it is reconfirmed that a full activation of low-dose implanted ions in both cases of arsenic (n-type) and boron (p-type) doping can be achieved in metastable Ge_xSi_{1-x} epilayers without relaxing the strain upon thermal annealing, and the difference of the electrical behavior in between n-type doped and p-type doped GeSi is discussed.

EXPERIMENT

1) Sample preparation

Undoped $Ge_{0.08}Si_{0.92}$ alloy layers were epitaxially grown on lightly doped ($2x10^{15}$ cm^{-3}) p-type Si (100) substrates by chemical-vapor deposition. Lightly doped n-type $Ge_{0.06}Si_{0.94}$ alloy layers were epitaxially grown at 525 °C on lightly doped ($2x10^{15}$ cm^{-3}) n-type Si (100) substrates in a molecular-beam-epitaxy chamber. The thicknesses of the $Ge_{0.08}Si_{0.92}$ and $Ge_{0.06}Si_{0.94}$ layers were 145±10nm and 260±10 nm, respectively as deduced from MeV ^4He backscattering spectra (we only show the spectra obtained from the $Ge_{0.08}Si_{0.92}$ layers in figure 1). (400) double crystal x-ray diffractometry on the as-grown $Ge_{0.08}Si_{0.92}$ shows a relative angle of -0.225 ° using Cu-Kα radiation (λ = 1.54Å) (Fig. 2). This value corresponds to a perpendicular strain of 0.58% and is consistent with a pseudomorphic $Ge_{0.08}Si_{0.92}$ layer on Si (100), based on elastic deformation theory [12]. The same diffractometry on the as-grown $Ge_{0.06}Si_{0.94}$ shows a relative angle of -0.167° for the GeSi peak using Cu-Kα radiation (λ = 1.54Å) (Fig. 3). This value corresponds to a perpendicular strain of 0.43 % and is also consistent with the strain expected in a pseudomorphic $Ge_{0.06}Si_{0.94}$ layer on Si (100).

2) Ion implantation and annealing

^{75}As ions of 90 keV energy were implanted to a low dose of $1x10^{13}$ cm^{-2} into the $Ge_{0.08}Si_{0.92}$ epilayers, and BF_2^+ ions of 70 keV energy were implanted to a low dose of $3x10^{13}$ cm^{-2} into $Ge_{0.06}Si_{0.94}$ epilayers. Both implantations were done at room temperature and lightly doped Si samples were also implanted under the same conditions for references.

According to the TRIM-92 simulation, the projected range and the straggle of 90 keV As ions are ~60 nm and 20 nm in $Ge_{0.08}Si_{0.92}$, respectively. The arsenic profile thus extends over the first two thirds of the epilayer and has an approximate As peak concentration of $2x10^{18}$ cm^{-3}. After the implantation, the samples were subjected to 30 min-long thermal annealing at temperatures of 500-900 °C in a tube furnace with a vacuum of about $5x10^{-7}$ torr, or to short 40 s annealing in a lamp furnace at 800, 850, or 900 °C with a nitrogen ambient at atmospheric pressure. For the implantation of BF_2^+ ions, the B^+ ion is implanted into $Ge_{0.06}Si_{0.94}$ with an energy of 15.7 keV since the atomic mass of a BF_2 is 49 while that of B is only 11, i.e. (11/49) x 70 keV = 15.7 keV. According to the TRIM-92 simulation, the projected range and the straggle of 15.7 keV B^+ ions are ~70 nm and 35 nm in $Ge_{0.06}Si_{0.94}$, respectively. The boron profile has an approximate peak concentration of $4x10^{18}$ cm^{-3} and exceeds the background doping concentration of $2x10^{15}$ cm^{-3} to a depth of 190 nm from the surface, which is less than the 260 nm thickness of the GeSi layer. The projected range and the range straggling in Si samples are almost the same as those in $Ge_{0.06}Si_{0.94}$ samples, according to the simulation. After the implantation, the samples were subjected to 30 min-long thermal annealing at temperatures of 550-900 °C in a tube furnace with a vacuum of about $5x10^{-7}$ Torr, or to short 10-40 s annealing in a lamp furnace at 700, 800, or 900 °C with a nitrogen ambient at atmospheric pressure.

3) Characterization

The damage and strain of the implanted GeSi layers before and after annealing have been characterized by 2.0 MeV $^4He^{++}$ backscattering/channeling spectrometry and by symmetrical (400) x-ray rocking curves taken with a double-crystal x-ray diffractometer. Plan-view transmission electron microscopy has also been used to reveal the dislocations caused by strain relaxation. Hall effect and sheet resistance measurements using the van der Pauw technique were also performed on these samples to determine their sheet carrier concentrations and mobilities. The percentage of electrically activated dopants was obtained by normalizing the measured sheet carrier concentration to the dose of implanted As ions [13]. The Hall factor for electrons in all samples was assumed to be unity in this work.

RESULTS

2.0 MeV $^4He^{++}$ channeling spectra obtained from the annealed samples of both $Ge_{0.08}Si_{0.92}$ and $Ge_{0.06}Si_{0.94}$ do not indicate strain relaxation, even after annealing at a temperature as high as 900 °C for 30 min. The spectra in figure 1 only show that the as-implanted $Ge_{0.08}Si_{0.92}$ samples achieve higher channeling yields than annealed samples due to implantation-induced defects. No significant difference is observed in either the Si or the Ge signals of the channeling spectra between long and short annealing. The minimum channeling yields of the virgin samples and of those annealed after implantation are low (~3.5%) and almost the same. Similar spectral results were found in the annealed samples of $Ge_{0.06}Si_{0.94}$.

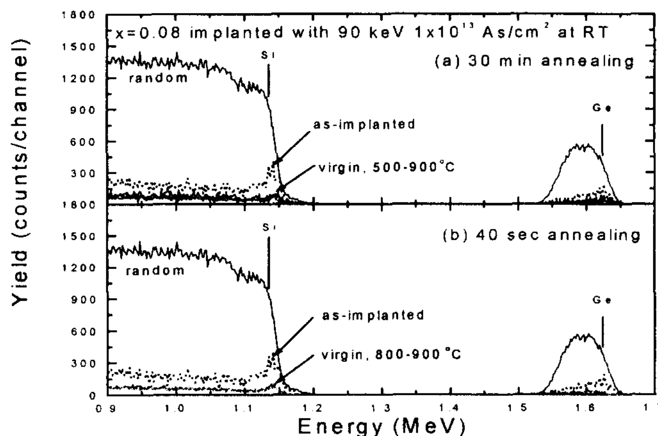

Figure 1. 2.0 MeV ^4He <100> channeling spectra for a metastable pseudomorphic $Ge_{0.08}Si_{0.92}$ layer grown on Si(100) implanted at room temperature with $1x10^{13}/cm^2$ 90 keV BF_2 ions.

Figure 2(a) shows the results of double-crystal x-ray diffractometry measurements on $Ge_{0.08}Si_{0.92}$ samples after long annealing for 30 min at 500 to 900 °C. The rocking curve of the as-implanted sample shows a larger negative angular shift than that of the as-grown sample, indicating that the implantation introduced additional compressive perpendicular strain in the film [14]. This additional strain disappears after annealing at 500 °C. The spectra of samples annealed between 500~700

°C have same epilayer peak intensity and the peak position as those of the as-grown (virgin) samples (-0.225 °). Unlike the results obtained from ion channeling measurements, the rocking curve for the sample after annealing at 800 °C shows clear signs of strain relaxation. At 900 °C annealing, the strain is substantially relaxed, but the peak position of the epilayer signal has not reached the position of a fully relaxed film (-0.13 °, indicated on the abscissa). This, and the much lesser signal intensity, mean that the film is quite defective and also contains threading dislocations through the film and down to the interface [15]. He channeling spectrometry is not sensitive enough to see this defective structure (detection limit $\sim 10^9$-10^{10} dislocations/cm^2), but rocking curves are (detection limit $\sim 10^6$-10^7 dislocations/cm^2) [5]. After a 40 s short annealing (Fig. 2(b)), the pseudomorphic state persists up to at 850 °C At 900 °C, the strain slightly relaxes, and is similar to that observed after a long annealing at 800 °C. Similar results have been reported by Lie et. al. for low-dose P implantation of pseudomorphic metastable $Ge_{0.12}Si_{0.88}$ [5].

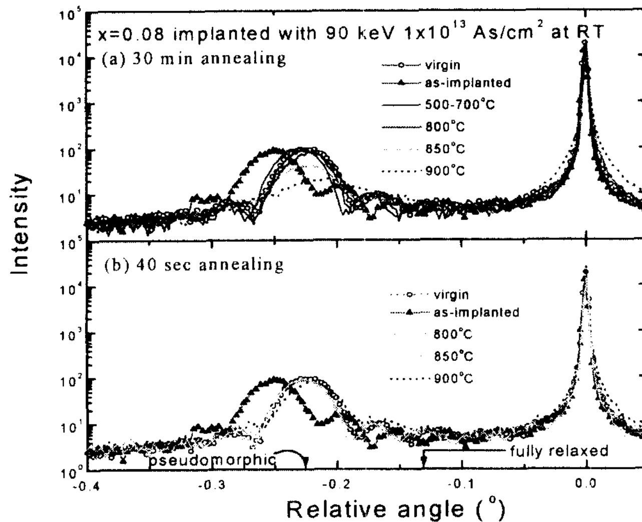

Figure 2. Double-crystal rocking curves of (400) symmetrical diffraction taken with Cu- $K\alpha$ radiation (λ=1.54 Å) for a metastable pseudomorphic $Ge_{0.08}Si_{0.92}$ layer grown on Si(100) implanted at room temperature with 1×10^{13}/cm^2 90 keV BF_2 ions.

Double-crystal x-ray diffraction spectra of the $Ge_{0.06}Si_{0.94}$ samples after annealing for 30 min at 550 to 900 °C are shown in Fig. 3(a). The angular shift of the GeSi peak for the as-implanted sample increases by about 5%, indicating that the implantation introduces additional compressive perpendicular strain in the film [14]. This additional strain disappears after annealing at 550 °C. The spectra of samples annealed between 550-800 °C have the same epilayer peak intensity and peak position as those of the as-grown (virgin) samples (-0.167 °). However, the implanted after annealing at 900 °C for 30 min show a clear sign of strain relaxation. The GeSi peak of the implanted layer shifts from the pseudomorphic position (-0.167 °) toward the full relaxation position (-0.1 °) by approximately -0.030 ° (~45% relaxation) while its intensity changes relatively little. After 10-40 s annealing (Fig. 3(b)), the pseudomorphic state persists, even at 900 °C.

The activation of the implanted As in the GeSi layer as obtained from Hall effect measurements after long 30 min or short 40 s annealing is given in Fig. 4. In both cases, full activation is achieved only after 900 °C annealing, but strain is altered at that temperature after 30 min (Fig. 2(a)). To maintain the strain unaltered with a 30 min-long annealing duration, the temperature has to remain below 800 °C. The maximum dopant activation percentage achievable is then only about 50% whereas a short 40 s annealing at 800 °C already achieves 85 % activation with the initial strain preserved. For the $Ge_{0.06}Si_{0.94}$ samples, the activation percentages of the implanted B in the GeSi layer as obtained from Hall effect measurements after a 30 min or a 10-40 s anneal are given in Fig. 5 (a) and (b) along with the sheet Hall mobilities of holes. We verified the presence of a p-n junction in the GeSi layer by displaying the rectifying characteristics of current flowing between the GeSi layer and the substrate, thus confirming that the Hall effect data do pertain to the implanted GeSi p-type layer. Figure 5 (a) shows that the activation percentage monotonically increases with temperature for 30 min annealing. Similar results are shown in Fig. 5 (b) for 40 s annealing and for durations increasing from 10 s to 40 s at 700 °C. In both cases, the full activation is apparently achieved only after annealing at 800 °C or higher. The apparent activation percentage achieved is 210 %. In the comparison Si sample doped under the same experimental conditions, the activation of dopants is 100 % (not shown in Fig. 5). The sheet value of the Hall mobility, μ_h, measured at full activation is

about 80 cm^2/Vs, which is lower than that of holes (125 cm^2/Vs) we have measured in the comparison Si with the same peak concentration of dopants ($4x10^{18}$ cm^{-3}, see the arrows in Fig. 5).

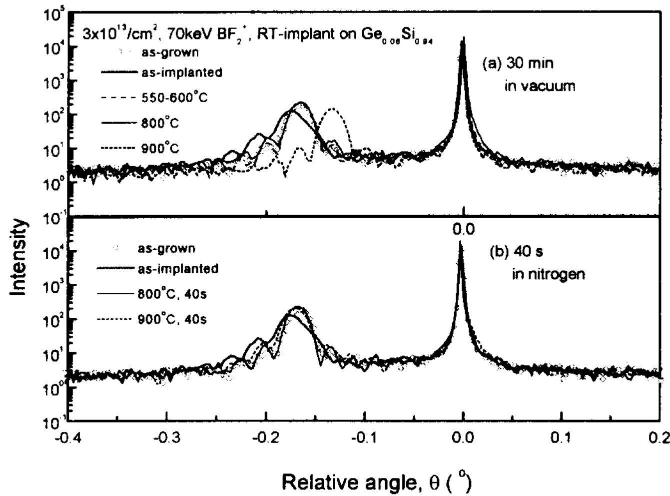

Figure 3. Double-crystal rocking curves of (400) symmetrical diffraction taken with Cu -$K\alpha$ radiation (λ=1.54 Å) for a metastable pseudomorphic $Ge_{0.06}Si_{0.94}$ layer grown on Si(100) implanted at room temperature with $3x10^{13}/cm^2$ 70 keV BF_2 ions.

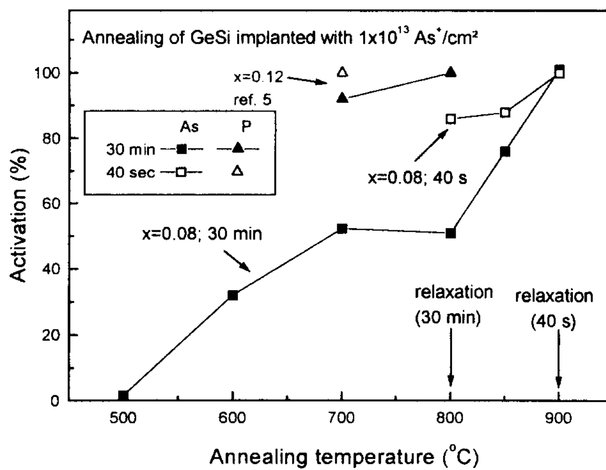

Figure 4. The ratio of electrons/cm^2 (obtained from Hall measurements) to As atoms/cm^2 implanted into the $Ge_{0.08}Si_{0.92}$ epilayer plotted as a function of the annealing temperature after the samples were annealed either in vacuum for 30 min each (solid squares) or in nitrogen for 40 s (open squares). Results from ref. [5] for P implantation are also included for comparison (solid triangles : 30 min, open triangles : 40 s).

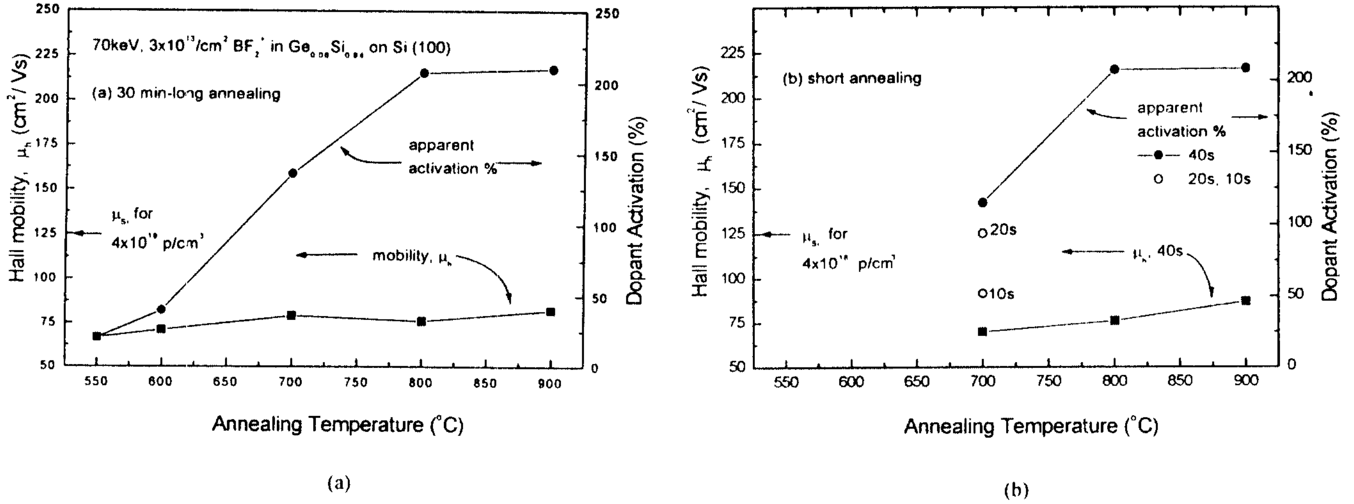

Figure 5. The sheet Hall mobility (squares) and the ratio of holes/cm^2 (circles, obtained from Hall measurements) to B atoms/cm^2 implanted into the $Ge_{0.06}Si_{0.94}$ epilayer plotted as a function of the annealing temperature after the samples were annealed: (a) in vacuum for 30 min each, and (b) in nitrogen for 10-40 sec. The sheet hole mobility in Si samples implanted and fully activated under the same experimental conditions is also indicated by arrows in Y-axis. The Hall factor for holes in all samples was assumed to be unity when converting the measured sheet Hall coefficient to sheet carrier concentration.

DISCUSSION

The sheet carrier concentration, p_S, in the implanted layer is given by ;

$$p_s = r_h/(q\ R_s),$$

where r_h is the Hall factor($\equiv\mu_h/\mu_d$), R_S is the sheet Hall coefficient, and q is the electronic charge [12]. The activation values in Fig. 4, Fig. 5 (a) and (b) were obtained by assuming r_h = 1. The activation of n-type dopants (As ions) shown in Fig. 4 seems to match the assumption. However, the activation behavior of the p-type dopants (B ions) in GeSi layers doesn't follow the assumption which leads to an erroneous result of 210% activation. If the activation is actually 100 %, as the constant activation above 800°C suggests, the sheet value of r_h (i.e. its value averaged over depth) in our samples (boron-doped $Ge_{0.06}Si_{0.94}$) can be obtained. The result is ~100/210 = 0.48. This value compares favorably with those we found in the literature: ~0.47 for a strained Ge_xSi_{1-x} layer with x = 0.08 and a doping concentration of $2x10^{19}$ cm^{-3} [11], and ~0.45 for a strained layer with x = 0.12 and a doping concentration of $1\text{-}2x10^{18}$ cm^{-3} [10]. Using 0.48 for r_h and the measured value of the sheet Hall mobility (~80 cm^2/Vs), the sheet value of the drift mobility, μ_d, of about 170 cm^2/Vs is obtained. This value of sheet hole mobility in $Ge_{0.06}Si_{0.94}$ is somewhat greater than the sheet mobility of holes of ~125 cm^2/Vs we measured on our silicon reference sample. Manku et al. reported similar results, where the in-plane drift mobility of holes in strained and uniformly-doped GeSi films was enhanced over that in Si [16].

The results for As ion-implantation into strained $Ge_{0.08}Si_{0.92}$ layer shows that rapid annealing at 800-850 °C for 40 s is an optimum condition to activate the implanted As in the GeSi layers and preserve the initial strain as well. Further annealing introduces unwanted dislocations by strain relaxation and also reduces the activation. Even though the thickness of 145 nm of the $Ge_{0.08}Si_{0.92}$ layer well surpasses its equilibrium critical thickness which is about 40 nm as calculated with the model of Matthews and Blakeslee [17,18], Fig. 1 and 2 show that only a few dislocations nucleate and propagate in 40 s at 800-850 °C. This means that the time period of 40 s in that temperature range is too short to cause the nucleation and glide of misfit dislocations. On the other hand, most dopants are well activated in this short time frame. Similar results have been reported for low-dose P implantation [5].

The instability of the $Ge_{0.06}Si_{0.94}$ layers becomes apparent after annealing at 900 °C for 30 min, even though their metastability persists up to at 800 °C for 30 min or at 900 °C for 40 s (Fig. 3). It is not surprising that the epitaxial film undergoes strain relaxation, since according to the Mathews and Blakeslee model, the equilibrium critical thickness for the $Ge_{0.06}Si_{0.94}$ layers is only about 70 nm [17,18]. However, the absence of peak broadening in the rocking curve data for the samples annealed at 900 °C for 30 min is noteworthy and indicates that the density of the threading dislocations in the sample is quite small, which means that the BF_2^+-implanted $Ge_{0.06}Si_{0.94}$ layers have better crystallinity than the arsenic-implanted $Ge_{0.12}Si_{0.88}$ layers after relaxation. The density of misfit dislocations for the $Ge_{0.06}Si_{0.94}$ sample

annealed at 900 °C for 30 min was estimated as about 10^5 cm^{-2} from a survey by plan-view transmission electron microscopy. We also calculated the density of misfit dislocations from the observed shift of the GeSi peak in Fig. 3 and obtained 9×10^4 cm^{-2}, which is consistent with the transmission electron microscopy result.

CONCLUSION

We conclude that after implantation at room temperature of a pseudomorphic metastable GeSi epilayer with a low As dose (i.e. one that does not amorphize the GeSi), short annealing durations at an elevated temperature are advantageous because the dopants can be activated and the strain conserved, while longer annealing durations at a lesser temperature can not achieve such results. We have also observed in strained $Ge_{0.06}Si_{0.94}$ layers implanted with a low dose of BF_2^+ ions that the full activation of dopants is successfully achieved without relaxing the strain by annealing the samples at 800 °C for durations of 40 s and 30 min. In the $Ge_{0.06}Si_{0.94}$ layers, full activation is also achieved for annealing at 900 °C but strain relaxation is observed after 30 min of annealing whereas no relaxation is detected after a 40 s. During the thermal relaxation, the crystallinity of the epitaxial $Ge_{0.06}Si_{0.94}$ layer undetectably degrades, observed by x-ray rocking curves. We have also found that the Hall factor for holes in the strained $Ge_{0.06}Si_{0.94}$ layers is about 0.48. The actual sheet drift mobility of holes in the layers is thus estimated as 170 cm^2/Vs, a value that exceeds both the sheet Hall mobility of the holes (80 cm^2/Vs) in the strained layers and the sheet mobility of the holes in the comparison Si (125 cm^2/Vs).

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