MULTIPLE DOPING OF SILICON-GERMANIUM ALLOYS FOR
THERMOELECTRIC APPLICATIONS

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ABSRACT

Improved silicon-germanium alloys currently under development are expected to result in substantial mass and cost savings for space nuclear power systems due to improved thermoelectric figure of merit values. Recent experimental and theoretical efforts on n-type gallium phosphide doped silicon-germanium (SiGe/GaP) indicate significant gains in thermoelectric figure of merit values can be achieved by increasing the carrier concentration. Standard n-type SiGe materials are doped with phosphorus to levels somewhat beyond the solubility limit and are therefore limited in ultimate figure of merit values.   The excess phosphorus precipitates out over time resulting in a gradual decrease in the figure of merit.   An increase in the dopant solubility limit is expected to both slow the rate of degradation with time and result in higher initial figure of merit values as well.   Results are reported on an experiment to test this hypothesis in both n- and p-type zone leveled silicon-germanium alloys which have been simultaneously saturated with both phosphorus and arsenic.

1.   INTRODUCTION

Figure of merit values ($ZT = \sigma S^2 T/\lambda$, where σ and λ are the electrical and thermal conductivities, S is the Seebeck coefficient and T is the absolute temperature) 20%-30% higher than typical of standard silicon-germanium values have been recently reported for n-type alloys doped with gallium phosphide [1,2].   While existing silicon-germanium technology is particularly well suited to providing the reliable, long term electrical power required for space electrical power applications [3-5] the improved materials offer the distinct possibility of substantial cost and mass savings at the system level.

Early experimental work on the high temperature thermoelectric   properties   of   phosphorus   and arsenic doped silicon-germanium alloys indicate the figure of merit, and therefore the energy conversion efficiency, increases with increasing carrier concentration up to the maximum doping levels   achievable   [6,7].   Current silicon-germanium   alloys   for   thermoelectric devices, therefore, are saturated with dopant during manufacturing in an attempt to achieve the highest carrier concentration possible. Since the solubility of the dopants is a strong function of temperature [8], however, alloys saturated during the   manufacturing   process   are   in   fact supersaturated over most or all of the operating temperature range of the final device.   Indeed, the most significant degradation exhibited by devices manufactured from these materials is due to the precipitation of dopant over time [8-10],which can amount to about 10% power loss over the course of time.

The improved figure of merit values recently reported have been attributed to the higher carrier concentration levels achieved in these materials ($2 - 3 \times 10^{20}$ cm^{-3}) compared to prior materials ($1.0 - 1.5 \times 10^{20}$ cm^{-3}). While detailed analysis is not yet complete [11], three important benefits can be expected from the increased doping levels: 1) an increased electrical power factor values,   primarily   because,   at   current   doping levels, the high temperature Seebeck values are well above the theoretical optimum value of $2.k_B/e$ = 172 $\mu V/K$;   2) a decreased lattice component of the thermal conductivity due to the scattering of phonons by carriers;   and 3) a reduced ambipolar contribution to the thermal conductivity.   This last effect alone may be as large as $20 - 30\%$ at the   highest   temperatures   where   the   thermal excitation of minority carriers can dominate the heat transport.

Each of these three factors tend to increase the figure   of   merit   with   increased   carrier concentration.   Counter balancing these effects will be the expected reduction of the carrier mobility   and   the   expected   increase   in   the electrical component of the thermal conductivity. Nevertheless,   preliminary   estimates   suggest additional   improvements   as   large   as $40 - 50\%$ beyond the values already achieved in the figure of merit may be possible by increasing the carrier concentration alone [11].

The present paper is primarily concerned with a possible method for achieving higher carrier concentrations, that is, by simultaneously doping silicon-germanium alloys with phosphorus and arsenic. By altering the chemistry of the system in this way it may be possible to achieve stable, equilibrium carrier concentration levels considerably in excess of the values possible by doping with either phosphorus or arsenic alone. Moreover, recent thermodynamic modeling of the solubility of dopants in silicon-germanium supports this assertion [12]. Such a material can be expected to exhibit both the higher initial conversion efficiency resulting from the higher carrier concentration levels, and exhibit superior stability over time due to the higher equilibrium doping levels affording by the double doping.

2. EXPERIMENTAL PROCEDURE

Round shaped slices, approximately 12 mm in diameter and 1mm thick, were cut from phosphorus, arsenic and boron-doped zone leveled ingots. The good homogeneity of the starting material was tested by density measurement, chemical analysis and X-rays diffraction. The Si/Ge atomic ratio was quite constant along each ingot (±1%), throughout all the slices used.

The samples were mechanically polished and ultrasonically cleaned in alcohol prior any diffusion treatment or before electrical characterization. Hall carrier concentrations and electrical resistivities of the original n-type samples indicated their homogeneous doping levels, while some boron-doped samples showed more important variations and had to be selected accordingly.

All the diffusion treatments were carried out in a similar fashion. The samples, together with the diffusion source, a small quantity of the desired elemental dopant, were put at opposite ends of sealed quartz ampoules under vacuum (10^{-6} Torr in ampoules 13 mm in diameter and 330 mm long). Then the ampoules were placed into a two zone furnace, where the samples were held at a temperature of 1030 $^\circ$C for ten days, providing the sample saturation. Dopants were high purity grade (5×9) phosphorus and arsenic. The minimum weight amount of the source was determined according to the saturated vapor pressure temperature dependence data for the pure solid elements [13]. Temperatures of 547 $^\circ$C for arsenic and 370 $^\circ$C for phosphorus were used, to ensure a dopant vapor pressure of 100 Torr.

At the end of the diffusion experiment, the samples were quenched by dropping the ampoule in cold water. The condition of the samples was generally fair, except when occasionally the As diffusion led to small droplets of (Ge+As) melts on the surface, carefully removed by polishing. Different procedures were used to check the saturation level of the samples and the efficiency of our quenching rate in order to optimize the diffusion and to be able to compare our results with literature. Identical original samples from

the same ingot were diffused with phosphorus, in the same conditions stated above, but for different periods of time. A diffusion period of five day yielded similar results to a ten day diffusion, the carrier concentrations being within 5% of each other. A twenty days diffusion showed no further significant changes from the ten days experiment.

Characterization of the samples was achieved through Hall effect and electrical resistivity measurement at room temperature, while the more interesting samples were investigated through microprobe analysis (MPA, JEOL-733), to evaluate the doping content and identify possible second phase inclusions. Thus, the homogeneous atomic composition of the samples was demonstrated by analyzing twelve points at random on the surface, and also by similarly investigating the profile of their cross-section.

3. RESULTS AND DISCUSSION

3.1 n-type samples

Diffusion of phosphorus, arsenic or both phosphorus and arsenic were conducted on phosphorus-doped samples and arsenic-doped samples. In order to compare the various experiments we first used two sets of samples coming from two ingots, one P-doped and one As-doped, with the same Si/Ge ratio and almost the same undersaturated doping level ($\cong 4.4.10^{19}$ and $6.2.10^{19}$ cm^{-3}). The diffusion treatments were repeated several times to ensure the reproducibility of the results.

Table I presents the results of these experiments conducted on Si$_{70}$Ge$_{30}$ alloys , where n is the Hall carrier concentration, ρ is the electrical resistivity and μ_H represents the Hall mobility.

Table I.   P and As diffusion on n-type Si$_{70}$Ge$_{30}$.

Original dopant	Diffusion treatments		n 10^{19}cm^{-3}	μ cm^{2}V^{-1}s^{-1}	ρ mΩ. cm
1	–	–	4.4	71.4	1.97
2	P	–	7.8	62.5	1.28
3 P	As	–	17.4	45.5	0.78
4	P	As	18.0	42.6	0.81
5	P	P+As	19.7	45.7	0.69
6	–	–	6.2	59.8	1.68
7 As	P	–	11.3	52.5	1.05
8	As	–	20.9	34.8	0.86

Phosphorus diffusion in a phosphorus-doped sample (line 2) gives a much lower carrier concentration value than arsenic diffusion in an arsenic-doped sample (line 8). Indeed, there is a factor of two between these two diffusion treatments. The presence of arsenic atoms in the samples seems to significantly enhance the resulting number of carriers after diffusion, even

in the case of phosphorus diffusion in an arsenic-doped sample ($n = 11.3.10^{19}$ cm^{-3}, line 7, compared to a value of $7.8.10^{19}$ for phosphorus diffusion in a phosphorus-doped sample, line 2).

For an identical carrier concentration, compared to phosphorus doping, arsenic doping of Si/Ge samples results in a sensible deterioration of their electrical properties: an increase of the electrical resistivity and a decrease of the Hall mobility. So, it was interesting to carry on double doping experiments in order to get advantages from both doping elements. By first saturating P-doped samples with additional phosphorus, and then diffusing arsenic, one expected better results: high carrier concentration, good carrier mobility and low electrical resistivity. But because of the important loss of phosphorus atoms during the Arsenic treatment, the resulting electrical resistivity was still high ($\rho = 0.81$ mΩ.cm, line 4).

To compensate for the phosphorus loss during diffusion with arsenic, a small amount of phosphorus was added to the arsenic diffusion source. This diffusion treatment provided the best results on our set of Si$_{70}$Ge$_{30}$ samples. The carrier concentration is slightly lower than the arsenic diffused As-doped sample, but the electrical resitivity is 20% lower while the Hall mobility is 30% higher. The carrier concentration room temperature values of these quenched samples are significantly higher than the ones quoted on fully saturated n-type RCA samples (around 15.10^{19} cm^{-3}), for the same silicon to germanium ratio [6].

The electrical properties behaviour of our samples, whether diffused with phosphorus or arsenic, was expected. Indeed, carrier mobility in Si/Ge alloys [6] and pure Si has been reported lower in As-doped material than in P-doped material, the decrease being attributed to stronger ionized impurity and grain boundary scattering mechanisms [14].

However, for this particular silicon to germanium ratio, the large difference between the carrier concentration values obtained with phosphorus or arsenic doping did not agree with previously published data [6], where the phosphorus doping achieved slightly higher carrier concentration than arsenic doping.
In order to investigate this phenomenon and to understand the saturation process of the Si/Ge samples, microprobe analysis was used to measure the homogeneity of the doping and to identify the presence of possible second phase formation and dopant precipitation. Figures 1 and 2 show photomicrographs of two different samples, one P-doped, As-diffused and one As-doped, P-diffused..

Table II gives the atomic composition of some of the spots analyzed in figures 1 and 2 on second phase inclusions of As-diffused samples. The microinclusions present on the pictures are impurities-rich, and the ratios between the

different elements suggest the presence of compounds such as SiAs, SiAs$_2$, GeAs, GeAs$_2$, whose stability and existence have been discussed earlier [15]. Presumably, phosphorus-rich microinclusions (such as SiP or SiP$_2$) precipitate in heavily doped phosphorus diffused samples.

Table II. Impurity rich microinclusions compositions.

Point #	at% Si	at% Ge	at% As
1	26.56	12.82	60.93
2	14.70	44.31	40.99
3	2.88	48.87	48.25

Also, excluding any second phase inclusion, the content of doping elements of the one phase solid solution is always significantly higher than the value expected from carrier concentration measurements. This is a constant feature of all P-doped or GaP-doped Si/Ge alloys. This phenomenon called polytropy of the impurities [16] is attributed to the interaction between silicon or germanium with the dopants, which results in the formation of stable compounds and neutral complexes competing with the incorporation of impurity atoms on substitutional sites [17]. In heavily-doped silicon, theoretical and experimental work have shown the formation of SiP precipitates [18] and vacancies-associated complexes [19], like V[As]$_4$. This is supported by the discrepancy between the changes in carrier concentration and impurity content when comparing slow cooling and quenching at the end of the diffusion treatment. Indeed, the increase in carrier concentration by quenching cannot be due only to the increase in solid solubility. One has also to allow for some dissociation of neutral complexes, the electrically inactive fraction of the impurity atoms present in the one phase solid solution.

3.2 p-type samples

Boron-doped samples were investigated in two different ways. The first one was to try to overcompensate p-type samples with a low boron content ($p \cong 3.10^{19}$ cm^{-3}), by saturating them using phosphorus or/and arsenic diffusion. The aim of that approach was to use the association between boron and phosphorus or boron and arsenic in order to increase the solid solubility of the donor dopant, in an effort to improve the thermoelectric properties of the resulting n-type samples.

Such studies have been performed on Si or Ge doped with III-V compounds [20]. Moreover, it has been shown that ion pairing had an important effect in determining the diffusion and precipitation behaviour of impurities in highly doped silicon. Calculations of III-V ion pairing coefficients [21] have demonstrated the strong interaction occurring between boron and phosphorus ,arsenic or antimony, leading to a reduction in lattice distortion.
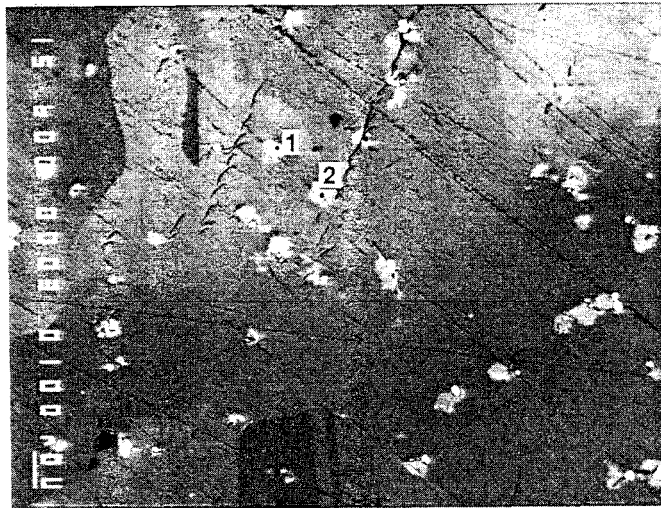
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Fig. 1. Phosphorus-doped $Si_{0.7}Ge_{0.3}$ diffused with arsenic.
Back-scattered electrons (x60)
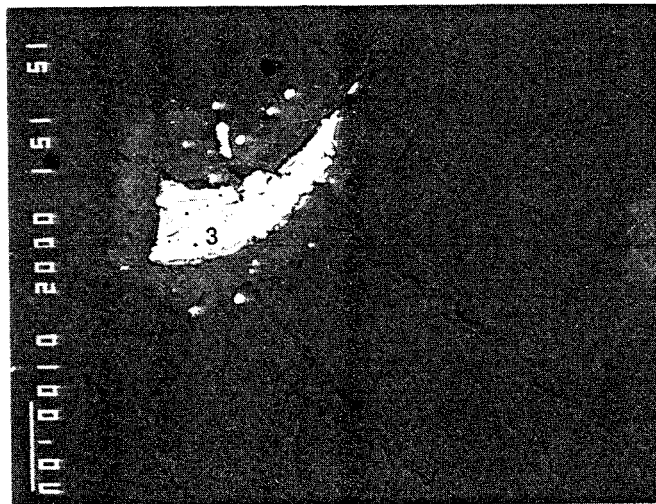

Fig. 2. Arsenic-doped $Si_{0.7}Ge_{0.3}$ diffused with arsenic.
Back-scattered electrons (x150)

The diffusion of phosphorus was conducted on several Si/Ge samples ranging from 65 at.% to 90 at.% of silicon. But even with the lowest boron doping level available, the diffusion treatment was unable to achieve overcompensation. The increase in electrical resistivity together with the sharp decrease of the Hall mobility show the deterioriation effect of impurity compensation on the transport properties. Table III displays the Hall measurement results (with the same units than in table I), on two B-doped $Si_{65}Ge_{35}$ before and after diffusion.

Table III.   Overcompensation of B-doped samples with P or As diffusion.

Dopant	Diffusion	n or p	μ	ρ	Type
B	– P	4.48 6.51	58.15 31.52	2.39 3.14	p p
	– P+As	3.39 16.77	53.59 41.86	3.43 0.89	p n

In a similar way to the experiments performed on n-type material, the incorporation of arsenic atoms by diffusion appears to be more efficient. We were able to overcompensate several samples, whose final electrical properties were close to the n-type As-diffused ones. Measurement and comparison as a function of temperature of the thermoelectric properties of Si/Ge alloys doped with either B,P and As or P and As only, are needed to determine any improvement of the thermoelectric figure of merit and the precipitation rate of the impurities.

From that point of view, it was of interest to reverse completely our approach, and investigate the diffusion of multiple dopants in heavily doped p-type samples. Using Si/Ge samples with a high boron content (carrier concentration up to 3.10^{20} cm^{-3}), the diffusion of donor dopants such as phosphorus or arsenic could lead to better thermoelectric properties and slower precipitation kinetics than in boron only doped p-type samples. The first experiments have shown that the overall properties values were little affected: the carrier concentration increased by 10% while the mobility and electrical resistivity remained stable. Again, thermoelectric characterization at high temperature is needed to investigate the III-V interaction.

4. CONCLUSION

Heavy doping of n-type Si/Ge alloys with phosphorus and arsenic (V-V doping interaction) through diffusion led to a significant enhancement of their carrier concentration, allowing possible improvement of the thermoelectric figure of merit.

High carrier concentrations were achieved by arsenic doping alone, but for a same doping level higher carrier mobilities and lower resistivities are obtained through phosphorus doping. By combining the two dopants with adequate diffusion treatments, we were able to optimize the different

properties: high carrier concentration, good carrier mobility and low electrical resistivity.

Similar experiments, using the III-V doping interaction, were conducted on boron-doped p-type samples and showed the possibility of overcompensating them by diffusing arsenic, in order to get n-type behaviour. Thermoelectric characterization as a function of temperature will permit to investigate and to compare performances of the different double doping combinations.

ACKNOWLEDGEMENTS AND REFERENCES

[1] J. W. Vandersande, C. Wood and S. L. Draper, Mat. Res. Soc. Symp. Proc. 97, 347 (1987).

[2] J. W. Vandersande, C. Wood, S. L. Draper, V. Raag, M. Alexander and R. Masters, Trnasactions of the Fifth Symposium on Space Nuclear Power Systems, Albuquerque, NM, 629 (1988).

[3] C. M. Bhandari and D. M. Rowe, Contemp. Phys., 21, (3), 219 (1980).

[4] D. M. Rowe, J. of Power Sources, 19, 247 (1987).

[5] C. Wood, Rept. on Prog. in Phys., 51, 459 (1988).

[6] J. P. Dismukes, L. Ekstrom, E. F. Steigmeier, I. Kudman and D. S. Beers, J. Appl. Phys., 35, (10), 2899 (1964).

[7] R. S. Erofeev, E. K. Iordanishvili and A. V. Petrov, Soviet Phys. Solid St., 7, 2470 (1966).

[8] L. Ekstrom and J. P. Dismukes, J. Phys. Chem. Solids, 27, 857   (1966).

[9] V. Raag, Proceedings of the Tenth Intersociety Energy Conversion Engineering Conference, 168 (1975).

[10] G. Stapfer and V. C. Truscello, Proceedings of the Seventh Intersociety Energy Conversion Engineering Conference, (1972).

[11] C. B. Vining, to be published.

[12] J. P. Fleurial, to be published.

[13] R. C. Honig and D. A. Kramer, RCA Review, 30, (2), 285, June   (1969).

[14] S. Solmi, M. Severi, R. Angelucci, L. Baldi and R. Bilenchi, J. Electrochem. Soc., 129, (8), 1811 (1982)

[15] Ya. A. Ugai, E. G. Goncharov, L. I. Sokolov and V. R. Pshestanchik, Neorg. Mater., 23, (7), 1090 (1987).

[16] V. I. Fistul , Heavily doped semiconductors (1972)

[17] A. Ya. Gubenko, Neorg. Mater., 20, (8), 1416 (1984).

[18] M. Servidori, C. Dal Monte and Q. Zini, Phys. Stat. Sol. (a) 80, 277 (1983).

[19] K. C. Pandey, A. Erbil, G. S. Cargill, III, R. F. Boehme and D. Vanderbilt, Phys. Rev. Lett., 61, (11), 1282 (1988).

[20] V. M. Glazov and V. S. Zemskov, Physicochemical principles of semiconductor doping, (1967)

[21] N. E. B. Cowern, Appl. Phys. Lett., 54, (8), February (1989).

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