Experimental Study of Diffusion and Segregation in a Si-(Ge_xSi_{1-x}) Heterostructure

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Experimental results have been obtained on the segregation coefficients of boron, phosphorus, and arsenic in the Si-(Ge_xSi_{1-x}) heterostructure. It is found that boron tends to segregate into the Ge_xSi_{1-x} layer, while phosphorus and arsenic tend to segregate away from it. The results are discussed within the framework of Hu's recent theory. The important factor is the "ideal work function" difference between two regions of the heterostructure; this difference can be estimated from the band-gap change and the band offsets. The effect of pseudomorphic strain energy is found to be appreciable for boron. Within experimental error, the diffusivities have not been appreciably affected.

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The semiconductor heterostructure has in the last several years attracted much research activity both on practical device applications and on the basic issues of misfit dislocations and band offsets. However, another important issue, the diffusion and segregation of dopants in heterostructures, has not been investigated. A basic understanding of this subject is essential for the prediction, control, and manipulation of dopant profiles in heterostructures in any routine and reliable device processing. To address this issue, the first step was taken by one of us in a theoretical paper [1,2] which was recently reformulated and extended [3]. There, various factors are analyzed that affect the diffusion and segregation of dopants in heterostructures. These factors are synthesized into expressions for the dopant chemical potential, segregation coefficient, and diffusion flux. The theory will provide the essential basis for the process modeling required in heterojunction device process development. But experimental results are needed, both for the verification of the theory, and to provide values of physical parameters. In this paper, we report, for the first time, experimental results on the diffusion and segregation of boron, phosphorus, and arsenic in the technologically important Si-(Ge_xSi_{1-x}) heterostructure. We will discuss the results in terms of the theory of Refs. [1-3].

Samples were prepared by epitaxially growing the Ge_xSi_{1-x} alloy layers on silicon substrates at 550 °C, using ultrahigh-vacuum chemical-vapor deposition. The setup and the operations are similar to those described in Ref. [4]. The substrates were 125-mm, 1-2-Ω cm, p-type silicon wafers. The heterostructure consisted of a 50-nm intrinsic silicon layer over a 70-nm layer of $Ge_{0.1}Si_{0.9}$ alloy layer on a silicon substrate. Dopants were diffused from a 200-nm polycrystalline silicon layer, which was implanted with a 2×10^{15} cm^{-2} dose of boron at 5 keV, phosphorus at 10 keV, or arsenic at 20 keV. Controls were prepared by using the same ion-implanted polycrystalline silicon on substrates without Ge-Si alloy layers. All samples were capped with 50 nm of plasma-enhanced chemical-vapor deposited SiO_2, and annealed at 950 °C with no temperature ramping. In order to produce a suitably deep profile for this study, the boron-, phosphorus-, and arsenic-doped samples were annealed for 1, 2, and 12 h, respectively. Dopant profiles were measured with a CAMECA 4F secondary ion mass spectrometer (SIMS), using implanted calibration standards to determine the impurity concentrations. SIMS quantification requires a uniform ion yield in both the sample and standard. A change in the matrix composition, in this case from Si to SiGe alloy, could affect this ion yield, giving incorrect concentrations in the 10% Ge region. To determine the effect of the matrix change, double implants of Ge and dopant species overlapping in the appropriate concentration range were profiled. The measured dopant distributions were found to be undisturbed by the 10% Ge. This indicates that the concentration change in the diffused dopant profile in the Ge/Si alloy is not an ion yield shift, but an actual change in concentration. The samples were examined by transmission electron microscopy. No misfit dislocation or other types of crystalline defects were found in the samples.

The dopant profiles in the heterostructures after the 950 °C anneal are shown as solid curves in Figs. 1-3, for boron, phosphorus, and arsenic, respectively. The dopant concentrations are graduated in atoms cm^{-3} on a logarithmic scale on the left vertical axes, and the germanium concentration is graduated in at.% on a linear scale on the right vertical axes. To afford more precise evaluations of the segregation coefficients, the boron, phosphorus, and arsenic concentrations on a linear scale are also shown in the insets of these figures; the corresponding germanium profiles are not shown. Dopant profiles in the control samples (silicon substrates without the germanium-doped layers) are shown as dotted curves, overlaid on the corresponding dopant profiles for the Si-(Ge_xSi_{1-x})-Si heterostructures.

The long anneal time of the arsenic-doped sample caused a substantial broadening of the germanium profile, as seen in Fig. 3. As a result, the peak concentration of germanium decreased from 10 to 8 at.%. Because an unusually large load was placed in our low-temperature vacuum deposition system, some of the wafers

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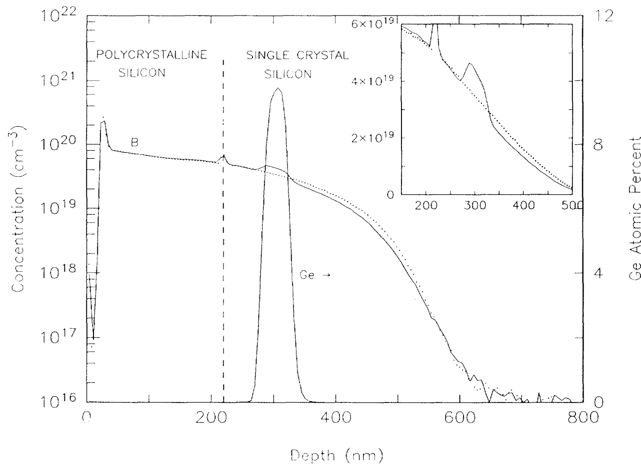

FIG. 1. Boron concentration profiles in germanium-doped (solid curve) and control (dotted curve) silicon. The germanium profile is not shown in the inset.

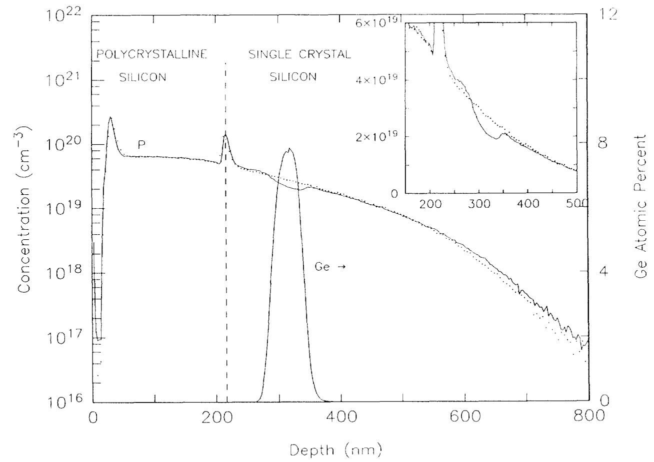

FIG. 2. Phosphorus concentration profiles in germanium-doped (solid curve) and control (dotted curve) silicon. The germanium profile is not shown in the inset.

were placed beyond the flat zone of the system. Consequently, there was also some nonuniformity of the initial germanium content among the samples. Some of the wafers had an initial germanium peak concentration as low as 8 at.%. This appears to be the case for the phosphorus diffused sample. The peak germanium concentration in the boron-doped sample is 9.5%. In any event, it is the final germanium peak concentrations, as measured by SIMS, that determines the measured segregation coefficients.

The experimental results show that boron tends to segregate into the Ge_xSi_{1-x} alloy zone, while phosphorus and arsenic tend to segregate out of it, and that the segregation coefficients of these two groups are almost exactly reciprocal—namely, 1.35 for boron, and 0.76 and 0.75 for phosphorus and arsenic, respectively. This translates into a net segregation enthalpy, ΔH_{seg}, of -0.033, $+0.029$, and $+0.030$ eV, respectively, if, for the moment, we ignore the preexponential factor. From this observation, it seems tempting to conclude that the segregation is mainly determined by the charge states of the dopants, and that acceptors would tend to segregate into the alloy, while donors would tend to segregate away from it. The theory of dopant segregation in heterostructures, given in Ref. [3], shows that the segregation enthalpy is quite dependent on the dopant concentration and the intrinsic carrier concentration. Explicit expressions for dopant segregation are derived from the general expression for two limiting cases of practical interest, for $N_1 \gg 2n_i$ and $N_1 \ll 2n_i$, respectively, where N_1 is the dopant concentration, and n_i is the intrinsic carrier concentration at the diffusion temperature. These expressions exhibit distinctively different functional dependences on physical parameters. While data are available on the intrinsic carrier concentrations of silicon and germanium at high temperatures [5], they are not very reliable. No such data are available for the GeSi alloy. If we estimate the intrinsic carrier concentration to be on the order of 10^{19} cm^{-3}, then we see that, with the dopant concentration also on the order of 10^{19} cm^{-3}, our experimental condition borders on these two limiting cases. The segregation coefficient for the case of $N_1 \gg 2n_i$ is, for the case of donors, given by [3]

$$k_{seg} = A \exp\left[\frac{-\Delta H_{seg}}{kT}\right] = \left[\frac{N_c(N_2)}{N_c(0)}\right]^{1/2} \exp\left[\frac{Z_1 \Delta W_i(N_2) + \Delta E_{b1}(N_2) - \theta\beta_1\beta_2 N_2}{2kT}\right], \tag{1}$$

where N_c is the conduction-band density of states; for the case of acceptors, this is replaced by N_v, the valence-band density of states. ΔW_i is the change in the "ideal work function" from silicon to the Ge_xSi_{1-x} alloy at the germanium concentration N_2. ΔE_{b1} is the corresponding change in the dopant binding energy, which may be assumed to be negligible. The last term in the exponent is the strain energy contribution to the dopant chemical potential. β_1 and β_2 are the lattice contraction coefficients for the dopant and germanium, respectively. The constant θ is given by [3]

$$\theta \simeq 2(c_{11} + 2c_{12})(1 - c_{12}/c_{11}). \tag{2}$$

Equation (1) also serves to define the preexponential factor and the enthalpy of segregation. For the case $N_1 \ll 2n_i$, the

segregation coefficient for donors and acceptors is given by [3]

$$k_{\text{seg}}=\left[\frac{N_c(N_2)N_v(0)}{N_c(0)N_v(N_2)}\right]^{Z_1/2}\exp\left[\frac{1}{kT}\left(Z_1\Delta W_i(N_2)+\Delta E_{b1}(N_2)-\theta\beta_1\beta_2N_2+\frac{\Delta E_g(N_2)}{2}\right)\right], \tag{3}$$

where $\Delta E_g(N_2)$ is the band-gap change from silicon to Ge_xSi_{1-x} at N_2.

The term ideal work function is used in Refs. [1,3] to mean a work function that is free of surface effects, and is equal to the negative of the intrinsic electron chemical potential. This parameter is not directly measurable on any known material. But the relative value, ΔW_i, of a pair of materials which are joined to form a heterostructure can be estimated by making use of Anderson's rule for heterojunction band lineup [6], which can be written equivalently as $\Delta E_c=\Delta(E_c-E_i)-\Delta W_i \simeq \frac{1}{2}\Delta E_g-\Delta W_i$, or $\Delta E_v=\Delta(E_v-E_i)-\Delta W_i \simeq -\frac{1}{2}\Delta E_g -\Delta W_i$. Here, ΔE_c and ΔE_v are the conduction and the valence-band offsets, and ΔE_g is the change in the band gap at a given Ge_xSi_{1-x} alloy composition from pure silicon. These values have been measured at room, or somewhat higher, temperatures; but none has been measured at 950 °C. Nonetheless, these values allow us to get a reasonable estimate of ΔW_i. For a 10%-Ge alloy, the band-gap change is about -0.072 eV [7,8] from pure silicon, and the valence-band offset is about $+0.074$ eV [7,9]. This would give an estimate of -0.034 eV for ΔW_i. A proportional value can be taken for ΔW_i in the 8%-Ge alloy. No elastic constants for the Ge_xSi_{1-x} alloy are available, so we assume that they can be reasonably approximated by those of silicon. We take the elastic constants of silicon at 950 °C from Burenko and Nikanorov [10], with $c_{11}=14.6\times10^{11}$ dyn cm^{-2} and $c_{12}=5.2\times10^{11}$ dyn cm^{-2}. We take the lattice contraction coefficient data for phosphorus from Celotti, Nobili, and Ostoja [11], and the more up-to-date data for boron and germanium from Herzog, Csepregi, and Seidel [12]. The lattice contraction coefficients are, respectively for phosphorus, boron, and germanium in silicon, -1.8×10^{-24}, -5.0×10^{-24}, and $+6.2\times10^{-25}$ cm^3/atom. From these, we obtain the values of the term $\theta\beta_1\beta_2N_2$ in Eq. (1) as -0.044 and -0.013 eV for boron and phosphorus, respectively. The lattice contraction coefficient for arsenic in silicon is negligible [13].

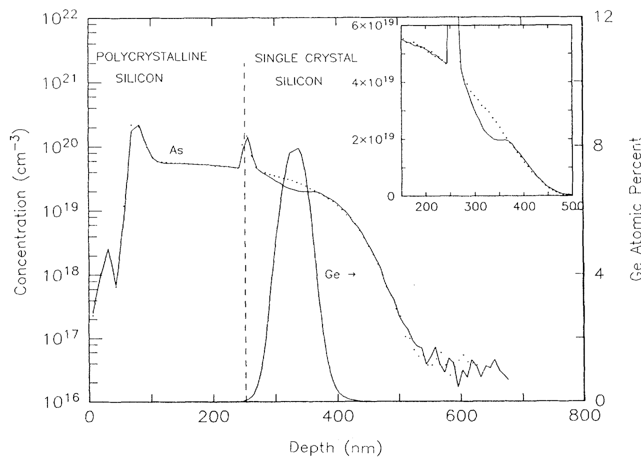

FIG. 3. Arsenic concentration profiles in germanium-doped (solid curve) and control (dotted curve) silicon. The germanium profile is not shown in the inset.

Because of the uncertainty in the experimental value of n_i, which puts the experimental condition approximately on the border of the two limiting cases, we shall first evaluate the segregation enthalpies for the dopants for these two limiting cases, and then take appropriate interpolations between them. For case 1, we obtain segregation enthalpies of -0.038, $+0.008$, and $+0.014$ eV, respectively, for boron, phosphorus, and arsenic in Ge_xSi_{1-x} layers of slightly different compositions taken from actual SIMS measurements. For case 2, the corresponding values are -0.041, $+0.051$, and $+0.064$ eV. We see that the mean values of the respective enthalpies from these two limiting cases are in reasonably good agreement with the corresponding experimental values of -0.033, $+0.029$, and $+0.030$ eV.

The preexponential factor has not been included in these calculations. The densities of states N_c and N_v in Ge_xSi_{1-x} may be assumed to be given by a linear interpolation between Si and Ge. At room temperatures, N_c is 2.8×10^{19} cm^{-3} for silicon, and 1.04×10^{19} cm^{-3} for germanium; N_v is 1.02×10^{19} cm^{-3} for silicon, and 0.61×10^{19} cm^{-3} for germanium [14]. They all increase with the 1.5th power of the absolute temperature and the temperature effect cancels out when taking ratios. With this assumption, we obtain, for case 1, the preexponential factors of 0.98 and 0.975 for acceptors and donors, respectively. For case 2, the corresponding values are 1.01 and 0.99. Inclusion of these preexponential factors will affect the segregation enthalpies only very slightly. We note also that the ionization energies of the dopant are not included in Eqs. (1) and (3). While they are present in the expressions of the electronic part of the dopant chemical potential given in Ref. [3], the effect of its variation with the alloy composition is negligible: The ionization energies for boron, arsenic, and phosphorus are, respectively, 0.045, 0.049, and 0.044 eV in silicon, and 0.0104, 0.0127, and 0.0120 eV in germanium [15]. Going from pure silicon to $Ge_{0.1}Si_{0.9}$, the ionization energy differences would be -0.0033, -0.0036, and -0.0032 eV, quite negligible. At higher dopant concentration, all these contributions to the enthalpy of segregation would be reduced by as much as one-half, because of the dopant self-potential

[3].

In conclusion, we have found that boron tends to segregate into the Ge_xSi_{1-x} alloy while phosphorus and arsenic tend to segregate away from it. The results indicate that the charge state of a dopant ion is an important factor affecting the dopant chemical potential. The band-gap change becomes another important factor at lower dopant concentrations. The external, pseudomorphic epitaxial strain energy plays an important role in the chemical potential of boron in Ge_xSi_{1-x}, but less significantly for phosphorus and arsenic. Overall, the results are in reasonably good agreement with Hu's theory [1,3]. Numerical simulations of dopant profiles were made by assuming abrupt Si-(Ge_xSi_{1-x})-Si zones, by taking the activity coefficient from the experimental segregation data, and by taking the same diffusivities for both the control and the germanium-doped samples. The closeness of the simulated profiles in both the control and the germanium-doped samples suggests that, within experimental error, the diffusivities of boron, phosphorus, and arsenic have not been significantly affected by the Ge_xSi_{1-x} layer.

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