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Observation of Boron and Arsenic Mediated Interdiffusion across Germanium/Silicon Interfaces

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The codiffusion of Ge with dopant atoms (boron or arsenic) into Si substrates is analyzed using secondary ion mass spectroscopy. While earlier studies have focused on the diffusion of dopants across deposited $Si_{1-x}Ge_x$ films or on diffusion phenomena at *in situ* doped $Si_{1-x}Ge_x/Si$ interfaces, this paper reports on the codiffusion of Ge and implanted dopant atoms into Si substrates resulting in the *in situ* formation of heavily doped $Si_{1-x}Ge_x/Si$ heterojunctions. The presence of dopants is seen to significantly enhance interfacial Si-Ge interdiffusion. The differences are discussed in light of the different diffusion mechanisms prevalent in the various heterojunction systems (undoped Ge/Si, p^+ Ge/Si, and n^+ Ge/Si).

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Dopant diffusion at $Si_{1-x}Ge_x/Si$ heterojunction interfaces has been studied earlier.[1-4] Such studies have focused on the anomalous diffusion of dopants, boron in particular, within $Si_{1-x}Ge_x$ films deposited on Si substrates. While a qualitative analysis of dopant diffusion across $Si_{1-x}Ge_x/Si$ heterostructures has been formulated, numerical values for the diffusion coefficients and activation energies of Ge, B, P, and As remain unknown. This study sheds light on the simultaneous diffusion of dopant atoms (B or As) and Ge atoms into Si substrates.

Experimental

Thin films of Ge (~600 Å) were deposited on 100 mm diam Si wafers (n- and p-type) in a conventional low pressure chemical vapor deposition (LPCVD) furnace using GeH_4 as the source gas. The deposition temperature was 340°C and the pressure was 600 mT. Ge films deposited under these conditions are expected to be polycrystalline.[5] A screening layer of SiO_2 (200 Å) was then deposited over the Ge film at 450°C. Appropriate dopants were implanted into the Ge in order to form p^+/n and n^+/p heterojunctions. A ^{+13}B dose of 5×10^{15} atoms/cm^2 was implanted at 5 keV, while an identical dose of ^{+75}As ions was implanted at 35 keV. The implants were designed to contain the implanted dose within the deposited Ge films. After implantation, a solid phase crystallization (SPC) anneal (350°C, 6 h) was performed. This step was included in order to ensure that any implant damage within the Ge film was annealed out before the high thermal budgets used for Ge-dopant codiffusion. It would thus be fair to ignore the effects of implantation induced vacancies or other point defects during the Ge-dopant codiffusion and to attribute the results only to effects inherent to the particular system involved. The SPC anneal was followed by high temperature rapid thermal annealing (RTA) at 300° and 900°C (1 min and 2 min). After high temperature annealing, secondary ion mass spectrometry (SIMS) analysis was used to profile Ge and dopant diffusion into the Si substrate. A Cameca-4f double focusing magnetic sector mass spectrometer with a Cs^+ ion beam was used for the SIMS analysis.

Results

Figure 1 shows the SIMS concentration-depth profiles after undoped Ge diffusion into Si at 900°C. Negligible diffusion of Ge is observed even after a 2 min RTA at 900°C. A remarkably abrupt diffusion profile is observed after each annealing step. Interestingly, the slope of the diffusion profile is unchanged and instead of flattening out, the interface is seen to shift and consume the Si. In addition, no signs of a pileup at the original Ge/Si interface are evident and Si-Ge interdiffusion is limited to the interfacial region. As a result, a fairly uniform Ge content is observed through the bulk of the film.

Ge is observed to display significantly different diffusion characteristics when codiffused with B. As shown in Fig. 2, the Ge profiles after annealing at 900°C display a slight pileup at the original Ge/Si interface. Several features become evident on a closer examination of the diffusion profiles. It can be seen that Si diffuses across the entire Ge film thickness. The Ge atomic concentration is seen to vary almost linearly from ~80% at the top surface to ~50% at the bottom interface. A pileup of Ge is evident at the interface and is seen to persist with increased time at high temperature, indicating a possibility of Ge segregation at the interface. The above observations indicate that Si-Ge interdiffusion is significantly altered in the presence of B. Ge and B also display strong correlation in their diffusion behavior. The B profile is completely contained within the Ge profile and also displays a pileup at the interface similar to the Ge profile.

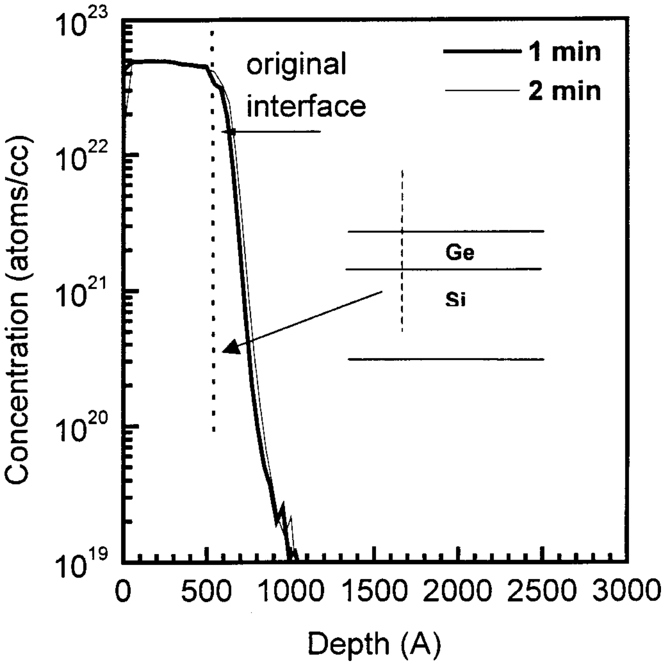

Figure 1. Ge diffusion profiles after rapid thermal annealing at 900°C. The Ge profiles are very abrupt with Si-Ge interdiffusion limited to the interface region.

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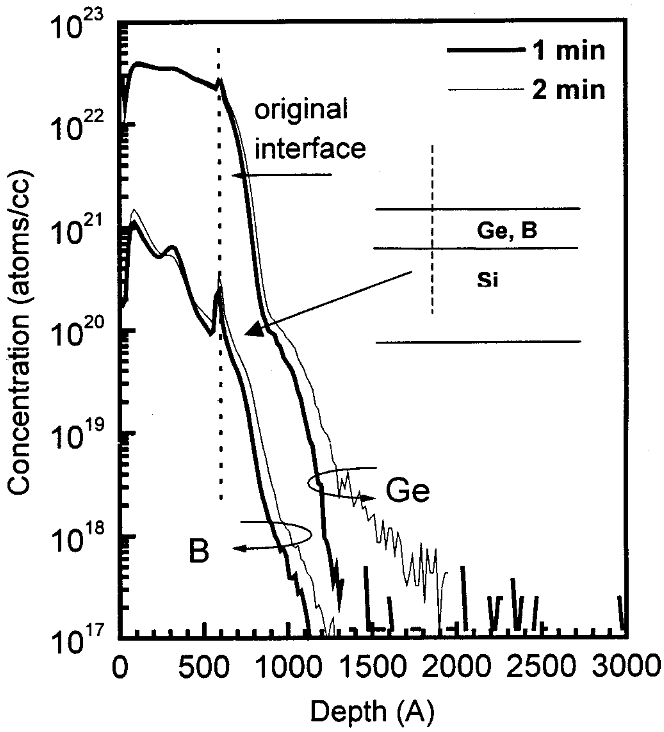

Figure 2. B and Ge diffusion profiles after rapid thermal annealing at 900°C. Extensive Si-Ge interdiffusion is observed accompanied by B and Ge segregation at the interface.

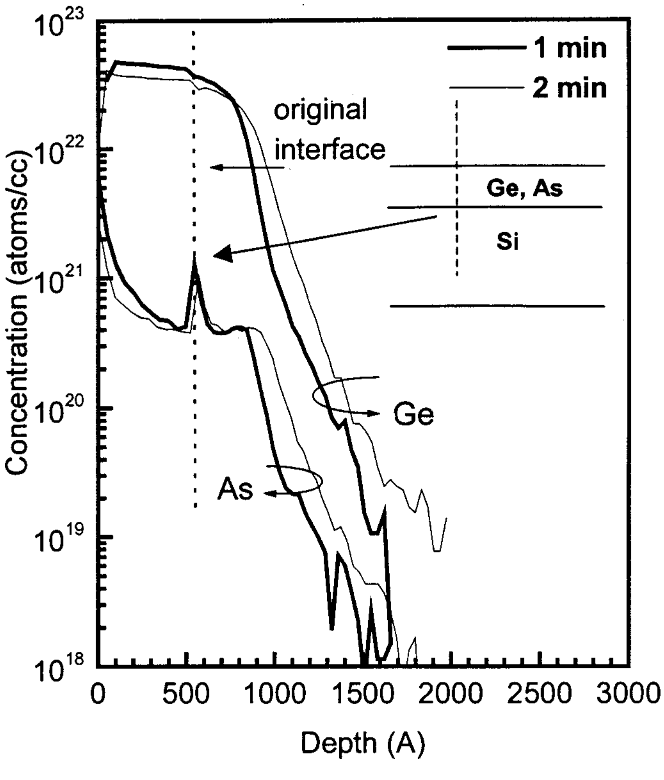

Figure 3. As and Ge diffusion profiles after RTA at 900°C. Significant interdiffusion of Si and Ge is observed. A pileup of As at the original interface is accompanied by a slight depletion in the Ge concentration profiles.

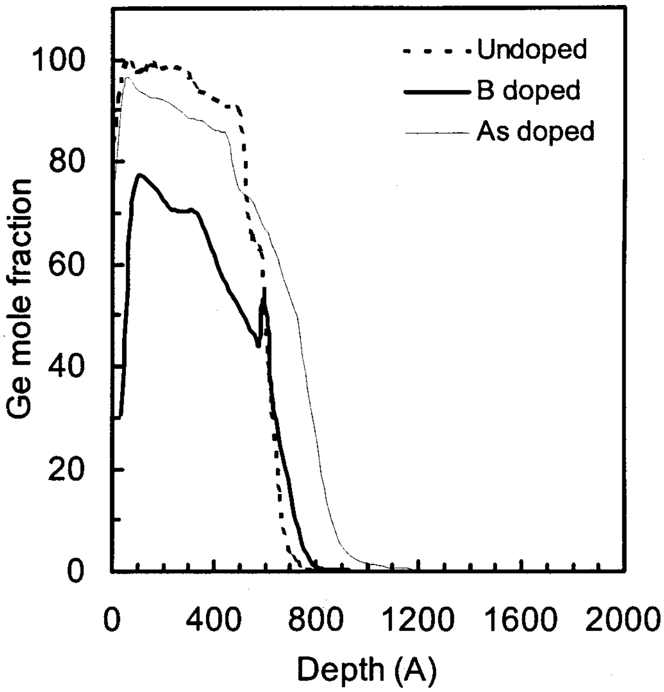

Figure 4. Ge diffusion profiles after a 2 min RTA at 900°C (undoped, B doped, and As doped). Undoped Ge displays minimum diffusion and intermixing, while As-doped Ge displays the maximum diffusion. B-doped Ge displays the maximum degree of intermixing.

Figure 3 shows the SIMS profiles for Ge and As codiffused into Si. It is observed that Ge diffusion into the Si is significantly enhanced by the presence of As as well. In addition, complete Si-Ge interdiffusion was observed leading to a linear variation in the Ge content throughout the film. The As diffusion profiles display a strong pileup at the position of the original interface while the Ge diffusion profiles show a slight depletion at the corresponding location.

Analysis

Interdiffusion at crystalline Ge/Si interfaces is believed to be mediated by the vacancy mechanism.[6,7] A 4.2% lattice mismatch between crystalline Ge and Si lattices is believed to create a significant density of point defects at the interface. The activation energy for Ge diffusion into Si (~5 eV)[8] is much higher than that for Si diffusion into Ge (~3 eV).[9] As a result, the upward migration of Si into the Ge film is believed to be the primary diffusing flux at the interface.[7] The upward flux of Si promotes a vacancy-assisted reciprocal migration of Ge atoms into the Si substrate. The net migration however has a high activation energy and is limited to the interfacial region. Csik *et al.*[10,11] have used several experimental techniques to analyze interdiffusion at amorphous Si-Ge interfaces. They also observe that interdiffusion is strongly asymmetric with very little Ge diffusion into Si and relatively fast diffusion of Si atoms into Ge. They attribute this effect to a strong concentration dependence of the interdiffusion coefficient in the amorphous Si-Ge system.

Hu *et al.*[2,12] have formulated the expressions for the segregation coefficients of dopants diffusing across Si$_{1-x}$Ge$_x$/Si heterojunctions. From thermodynamic arguments, they define the segregation coefficient as a function of the dopant charge, the density of states in the conduction and valence bands, strain and binding energy contributions, and the energy associated with the addition of an electron or a hole to the system. They observe that acceptor impurities tend to segregate in the Ge rich regions of a heterostructure while donor impurities tend to segregate in the Si rich regions. In their analysis, they considered diffusion across an existing heterojunction (thin

Table I. Diffusion coefficients (cm^2/s) for B, As, and Ge under the conditions studied. Values in italics are from this work. Others are from literature.[13]

	D_{Boron}	D_{Arsenic}	$D_{\text{Germanium}}$
In silicon	3.9×10^{-16}	$\sim 1.0 \times 10^{-17}$	*1×10^{-15}*
In germanium	2.1×10^{-11}	$\sim 1.0 \times 10^{-10}$	-
Codiffusion in Si	*4.0×10^{-15}*	*1.5×10^{-14}*	*With boron:* *4.7×10^{-15}* *With arsenic:* *1.9×10^{-14}*

$Si_{1-x}Ge_x$ layers embedded into a Si matrix). In the present experiment however; B, Ge and Si fluxes are concurrent, B diffusion is faster in Ge than in Si,[13] and a pileup of B is seen at the crossover into the Si-rich substrate. The enhanced interfacial diffusion leads to complete intermixing between Si and Ge. Also, note that an increased thermal budget slows down diffusion at the interface. Csik *et al.*[10] have experimentally observed a slowing down of intermixing between undoped Si and Ge after very long annealing times (increasing Si content within the Ge film). In the case of As-mediated interdiffusion, the fairly rapid diffusion of As in Ge promotes the downward flux of Ge atoms. However, from the thermodynamic argument in Ref. 12, As atoms should prefer to segregate within the Ge-deficient regions. The continued downward flux of Ge thus slows down the diffusion of As atoms. A pileup of As atoms is observed in the vicinity of the original interface and is accompanied by a corresponding depletion in the Ge profiles. The degree of Si-Ge intermixing is lower than in the case of B leading to a higher average concentration of Ge across the thickness of the film. From the SIMS profiles of Fig. 3 it is evident that the As follows the Ge into the Si and pushes it even deeper.

The effects of dopants on the diffusion behavior of Ge can be most clearly seen in Fig. 4, which compares the variation in the Ge mole fraction with depth for the three cases. By using the SIMS concentration depth profiles shown (900°C, 1 min and 2 min), the approximate diffusion coefficients for Ge, B, and As at 900°C have been calculated assuming simple Fick's law-type diffusion ($x = 2\sqrt{Dt}$) and reported in Table I. It should be noted that error associated with the depth measurement of craters left from SIMS sputtering (~10%) limits the accuracy of these values.

Summary

The interdiffusion of B- or As-implanted Ge thin films into Si substrates results in highly doped p^+/n or n^+/p heterojunctions. In both cases, the dopants are contained within the diffused $Si_{1-x}Ge_x$ layer. The codiffusion of Ge with dopants also leads to enhanced intermixing between Si and Ge.

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