

Silicon diffusion at polycrystalline-Si/GaAs interfaces

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Polycrystalline-Si/GaAs interfaces have been prepared by depositing hydrogenated amorphous Si (*a*-Si:H) onto GaAs in a silane plasma at 450 °C and annealing at temperatures between 600 and 1020 °C. Rutherford backscattering, secondary ion mass spectroscopy, and transmission electron microscopy show that the resulting polycrystalline-Si/GaAs interface is metallurgically stable when the Si is undoped while significant interdiffusion occurs when 12 at. % As is added to the Si. The data are consistent with the Greiner/Gibbons theory [Appl. Phys. Lett. 44, 750 (1984)] that high concentrations of Si diffuse in GaAs in the form of Si-Si substitutional pairs via Ga and As vacancies.

The diffusion and *n*-type activation of Si in GaAs are affected by surface conditions that promote the formation of Ga vacancies. For example, the diffusivity and activation are proportional to As vapor pressures,^{1,2} a direct function of Ga vacancy concentrations. Silicon dioxide is permeable to Ga and when used as a capping layer higher Si implant activations are obtained as compared with a Si₃N₄ cap which is impermeable to Ga and As.^{3,4} A thin (10 nm) Si layer electron beam deposited on GaAs produces a metallurgically stable interface if annealed with a Si₃N₄ cap but when SiO₂ caps are employed Ga diffuses from the substrate creating Ga vacancies. The result for SiO₂ caps is high concentration diffusion of Si into the GaAs.⁵ In this letter we describe an experiment aimed at the control of Si diffusion and activation in GaAs by the addition of As to a deposited layer of hydrogenated amorphous silicon (*a*-Si:H). We show that after annealing, the resulting polycrystalline-Si/GaAs interface (henceforth called Si/GaAs) is metallurgically stable when the Si is undoped but significant interdiffusion occurs when As is added to the Si. The data will be shown to agree well with the Greiner and Gibbons proposal that the dominant diffusing species of high concentration Si in GaAs is the substitutional and neutral Si-Si pair, diffusing via Ga and As vacancies.⁵

Films of *a*-Si:H were deposited by plasma enhanced chemical vapor deposition in a silane (SiH₄) plus Ar plasma (10% SiH₄) onto polished GaAs [semi-insulating, liquid encapsulated Czochralski (LEC), <100>] and thermally oxidized Si substrates. The substrates were used, as received from the manufacturer but were cleaned in an Ar⁺ plasma *in situ* prior to the Si depositions. Substrate temperatures during deposition were 450 °C. Arsenic was added to the silicon by mixing arsine (AsH₃) with the silane in the ratio 1 to 24. All depositions and experiments were run in parallel with samples from both substrate types. Film thicknesses were typically 100 nm.

Rapid thermal annealing to temperatures of 900–1020 °C for 10 s was carried out by a flash lamp system in

flowing Ar/H₂. The temperature was monitored with a thermocouple attached to the Si sample stage. Foils for cross-sectional transmission electron microscopy (TEM) were prepared by ion milling 50-μm-thick sections (4 keV, 40 μA). To study outdiffusion and composition, samples were analyzed by Rutherford backscattering spectrometry (RBS) with 3 MeV He⁺⁺ and Auger sputter profiling. Hydrogen content was measured with He⁺⁺ recoil analysis (75° tilt angle). After plasma etching the deposited Si in SF₆, the total concentration of Si diffused into the GaAs was measured by secondary ion mass spectroscopy (SIMS) using Cs⁺ primary ion bombardment and negative secondary ion detection. The profiles were calibrated using a Si implant standard.

The films deposited on thermal SiO₂ were visibly smooth before and after annealing. The majority of the surface area of films deposited onto GaAs was smooth, but randomly spaced bubbles, indicative of compressive stresses in the film, developed after annealing. However, the density of these bubbles did not interfere with the interface analysis undertaken in this work. Cross-sectional TEM confirmed that the Si crystallized and that the interface remained planar. The As composition of the as-deposited films was 12 at. % which was four times the atomic composition in the gas phase. Examination of the electron diffraction patterns of the Si before and after annealing did not reveal any phases other than Si. In particular, neither SiAs₂ (cubic, *A*₀ = 6.0252 Å) nor SiAs (monoclinic) was detected. Crystalline defects appeared in the top 200 Å of the GaAs which may have been the result of the high concentrations of Si diffusion into the substrate during annealing. Hydrogen content before annealing was about 5 at. % and was not detected with recoil analysis after annealing (< 1 at. %).

Figure 1 shows Auger sputter depth profiles of the Si-As/GaAs interface as deposited and after rapid thermal annealing at 1000 °C for 10 s. Ga is detected in the annealed Si-As film to levels of 2.1 at. % which increases towards the substrate to 2.6 at. %. Gallium has diffused from the substrate into the film. Rutherford backscattering and Auger

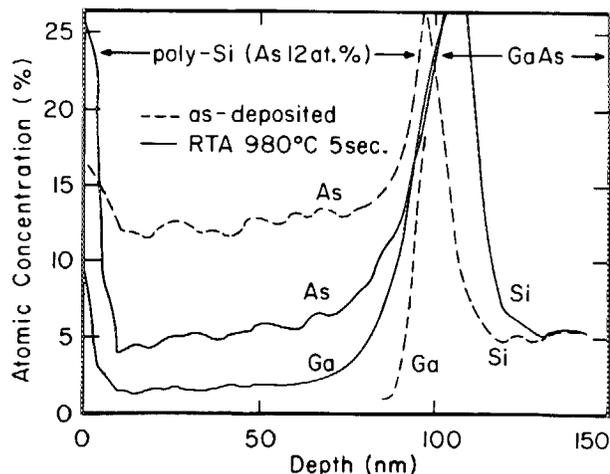


FIG. 1. Auger depth profiles of undoped and polycrystalline-Si + 12 at. % As/GaAs interfaces after rapid thermal annealing at 1000 °C for 10 s.

analysis showed that As evaporated from the film. Arsenic may also have diffused from the substrate but this is obscured by the As already present in this film. Gallium or arsenic outdiffusion from undoped *a*-Si/GaAs interfaces was not detectable. Diffusion of Si into the GaAs, in conjunction with the Ga (and possibly As) outdiffusion, was detected by SIMS. Figure 2 shows Si diffusion into GaAs for the As alloy and for undoped Si as a function of anneal temperature. In the case of the Si(As-12 at. %)/GaAs interface, Si diffused into the GaAs to a depth of 0.260 μm , with a surface concentration of 1×10^{20} atoms/cm³, after a rapid thermal anneal at 1000 °C. Some Si diffusion may be occurring from the undoped layers but the concentration is at least two orders of magnitude less than for the Si-As alloy interface.

The SIMS profiles do not follow error function curves, as they would if the diffusion coefficient was a constant. Assuming that the diffusivity of Si is independent of position or time and that the surface Si concentration is constant, we may use a Boltzmann–Matano analysis to extract a diffusion coefficient as a function of Si concentration from these pro-

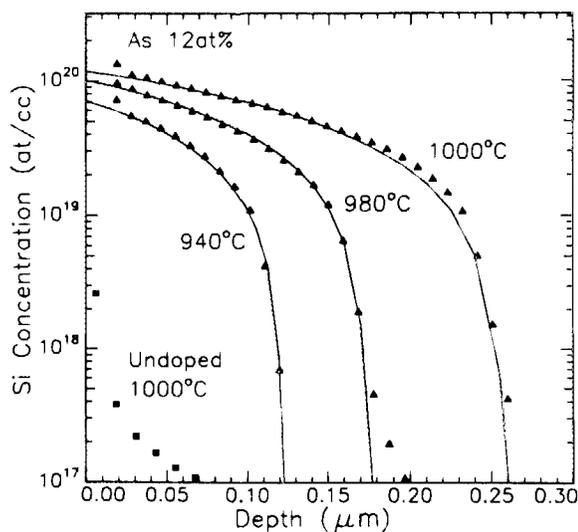


FIG. 2. Secondary ion mass spectroscopy (SIMS) profiles of Si diffusion into semi-insulating GaAs from polycrystalline-Si/GaAs interfaces after rapid thermal anneals for 10 s. The solid lines are calculated profiles from the Greiner/Gibbons theory.

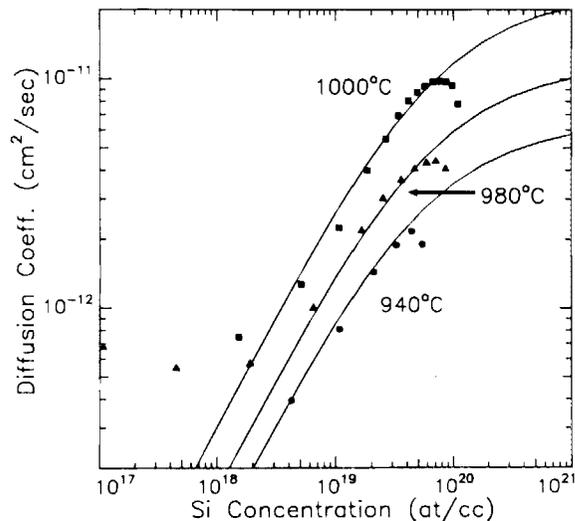


FIG. 3. Boltzmann–Matano analyses of the As-Si/GaAs SIMS data in Fig. 2. The solid lines are calculated from the Greiner/Gibbons theory.

files.⁶ Since integration of the diffusion profiles showed that less than 1 nm of Si diffused into the GaAs we therefore took the Matano interface to coincide with the Si/GaAs interface. Results of the Boltzmann–Matano analyses of the SIMS data of Fig. 2 are shown in Fig. 3. In each case, the diffusion coefficient increased with increasing Si concentration to a maximum, and at the highest concentrations, leveled off.

According to the Greiner/Gibbons model Si diffusion in GaAs occurs via the vacancy diffusion of substitutional single Si atoms and Si-Si pairs. The diffusion coefficients of each of these species are assumed to be independent of their concentration but since the Si-Si pairs are electrically neutral, they diffuse faster. At equilibrium, the concentration of Si-Si pairs is related to the concentration of single Si atoms by a mass action law $[\text{Si}_{\text{Ga}}][\text{Si}_{\text{As}}] = K_p[\text{Si}_{\text{Ga}} - \text{Si}_{\text{As}}]$, where K_p is the equilibrium constant for pair formation. After some calculation, the model predicts a concentration-dependent diffusion coefficient given by

$$D_c = D_{\text{pair}} [1 - (1 + 2[\text{Si}]/K_p)^{-1/2}], \quad (1)$$

where D_{pair} is the diffusion coefficient of Si-Si pairs and $[\text{Si}]$ is the total Si concentration. It follows from this equation that D_c is proportional to $[\text{Si}]$ for $[\text{Si}] \ll K_p$ and is equal to D_{pair} when $[\text{Si}] \gg K_p$.

Under the assumption that the Si pairs dominate the diffusion at high concentrations and that the pair diffusion coefficient is constant, Fickian diffusion was numerically simulated using D_c from Eq. (1). (See Ref. 5 for details.) Greiner/Gibbons estimates of K_p ($H_f = 0.46$ eV) were used for these calculations, the diffusion time was known from the experiment and the Si surface concentration was taken from the SIMS data. The only unknown parameter, the pair diffusion coefficient, was varied to obtain the best fit. The resulting profiles are found overlaid with the data in Fig. 2. The agreement is excellent.

D_c as a function of $[\text{Si}]$ was calculated from Eq. (1) using the values for D_{pair} obtained from the fits for each profile. The results have been overlaid with the Boltzmann–Matano data of Fig. 3. Our data are consistent with the predicted behavior. At Si concentrations less than 10^{18} cm⁻³ where

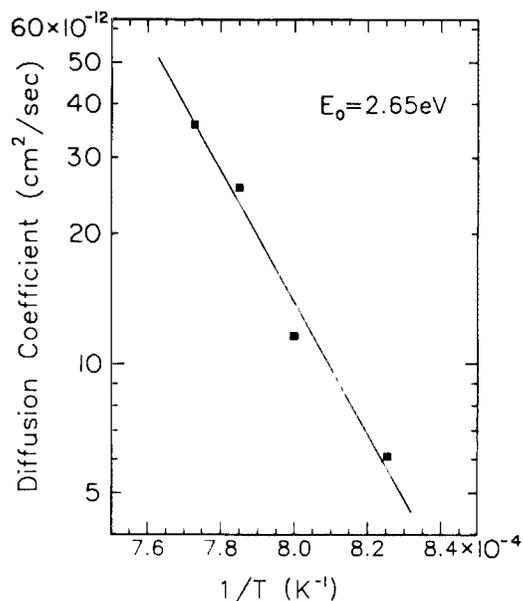


FIG. 4. Arrhenius plot of pair diffusion coefficient vs reciprocal temperature for Si diffusion in GaAs from a polycrystalline-Si(As 12 at. %) overlayer. The activation energy for Si-Si pair diffusion in GaAs was 2.65 ± 0.25 eV.

the diffusion coefficient is constant, the dominant diffusing species are single Si ions. As [Si] increases the concentration of Si pairs increases and the slope of D_c vs [Si] approaches unity. The unexpected leveling off observed at high concentrations may be related to a saturation in the concentration of Si pairs due to solid solubility limits. This would reduce the concentration gradient in the Si-Si pairs and result in a lower D_c .

To obtain the activation energy for the diffusion of Si-Si pairs, D_{pair} was plotted versus $1/T$. As shown in Fig. 4 a straight line can be drawn through the data giving an activation energy of 2.65 ± 0.25 eV. This is comparable to the activation energy for the Si diffusion from the SiO_2 capped layers (2.5 eV).⁵

We believe that the GaAs dissociated and outdiffused

primarily into the grain boundaries of the Si. A flux of Ga and As vacancies resulted allowing Si to diffuse into the GaAs. In view of the fact that any free As in the grain boundaries is molten at the annealing temperatures used, it is not surprising that the Ga and As diffused faster through the As saturated Si. However, a closer look at the Si grain boundaries would help to clarify the differences in the doped and intrinsic cases.

In conclusion, we have described the interdiffusion occurring at *a*-Si:H/GaAs interfaces. We have shown that, as previously reported for evaporated Si,⁵ interdiffusion is negligible or not detectable by SIMS or Auger analysis at undoped plasma deposited Si/GaAs interfaces after anneals at 1000 °C for 10 s. However, the present results indicate that deposited Si layers with incorporated amounts of As or possibly other dopants (e.g., phosphorus) can be used to control the diffusion of Si into GaAs. Si concentrations in the GaAs reached levels as high as 1×10^{20} atoms/cm³ with diffusivities in the range 5×10^{-13} – 2×10^{-11} cm²/s. The results were consistent with the Greiner/Gibbons theory involving vacancy diffusion of Si-Si pairs.⁵

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