Heavy doping of GaAs and AlGaAs with silicon by molecular beam epitaxy

M. Heiblum, W. I. Wang, L. E. Osterling, and V. Deline IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 17 June 1983; accepted for publication 12 July 1983)

Heavy Si doping of GaAs and AlGaAs grown by molecular beam epitaxy has been studied. By using a slow growth rate of 1000 Å/h, the electron concentration obtained for GaAs was $1.1\times10^{19}~\rm cm^{-3}$, which is higher than the previously reported limit of $5\times10^{18}~\rm cm^{-3}$. The accumulation of excess Si near the surfaces of GaAs and AlGaAs has been identified by secondary ion mass spectroscopy. A Si-induced 3×2 surface structure has been observed, and the influence of arsenic to gallium flux ratio on the surface morphology is discussed. Photoluminescence spectra of the doped layers are presented.

PACS numbers: 61.70.Tm, 68.55. + b, 81.15.Ef, 78.55.Ds

Heavy doping of epitaxial layers is very desirable since it eases the fabrication of low resistance ohmic contacts, and reduces the spreading resistance between contacts. Researchers always strive to achieve doping of about mid 10¹⁹ cm⁻³, since it enables the fabrication of nonalloyed ohmic contacts. Barnes et al. 1 and Tsang2 have reported on heavy doping with Sn of GaAs layers grown by molecular beam epitaxy (MBE). However, Sn dopant has a serious problem of segregation and surface accumulation due to surface rate limitation of incorporation.³ The results obtained using Sn are very sensitive to growth temperature and V/III flux ratio and not readily reproducible. Recently, Harris et al. have also studied heavily Sn-doped GaAs.4 They found that the highest free electron concentraton that could be achieved is 1.1×10^{19} cm⁻³. Any further increase in Sn flux merely resulted in greater surface aggregation of Sn. In any case, the results of heavy Sn doping are still highly controversial and further work is needed to clarify the doping limits of Sn. A more widely used n-type dopant is Si, which is less amphoteric than Ge, and has been found to be well behaved up to 5×10^{18} cm^{-3.5} Attempts to dope with Si to higher doping values requires cell temperatures which exceed 1250 °C, resulting in a large production of CO and N₂ from the Si cell (from the Ta filament and the pyrolitic boron-nitride crucible), which tends to compensate the *n*-type doping.

In this letter we report the results on Si doping of GaAs up to an average level of $1.1\times10^{19}~{\rm cm}^{-3}$ using a conventional MBE furnace, and on the accumulation of Si toward the surface at very heavy dopings. Photoluminescence results suggest that Si donor-acceptor pair complexes form at such high doping levels. In Si doped AlGaAs, Si accumulation near the surface occurs at a much lower doping level.

Epitaxial layers of GaAs and AlGaAs were grown by MBE in a Riber 1000-1 system. The growth procedure is described in Ref. 6. For all high doping experiments the Si effusion cells temperature was lower than 1250 °C to avoid CO and N_2 outgassing from the cell, but the growth rate was reduced to $\sim 1000 \, \text{Å/h}$. (Ga cell temperature was lowered to 847 °C.) GaAs layers 2000 Å thick were grown on top of a 2500 Å undoped buffer layer. When the Si cell temperature exceeded 1150 °C (corresponding to a doping density of $6 \times 10^{18} \, \text{cm}^{-3}$), the normal As stabilized 2×4 reconstructed surface, which is usually maintained with an approximate

As₄/Ga flux ratio ~ 1 , converted rapidly to a Si-induced 3×2 surface, and eventually to a Ga-stabilized $c(8\times 2)$ sur-

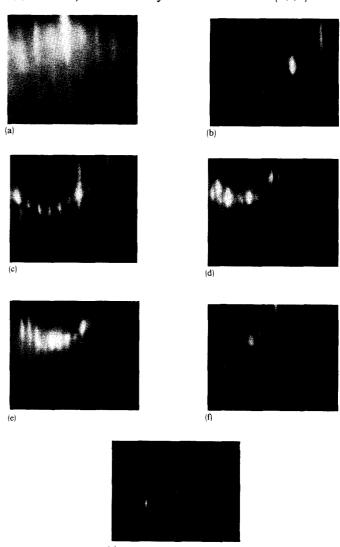


FIG. 1. Evolution of the RHEED patterns along [110] azimuthal direction. (a) 2×4 structure before starting Si doping with $As_4/Ga\sim1$. (b) Si-induced 3×2 structure after 60-Å growth of heavily Si-doped GaAs. (c) 3×2 structure after 120-Å growth. (d) Conversion from 3×2 to $c(8\times2)$ after 200-Å growth. (e) $c(8\times2)$ structure after 280-Å growth. (f) 3×2 structure after 300-Å growth, but with $As_4/Ga\sim5$. (g) The [110] azimuthal direction of (b)-(f).

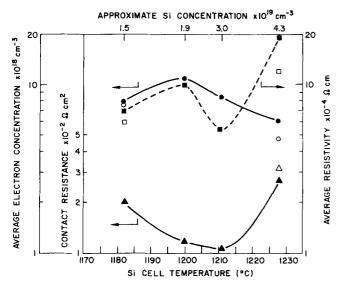


FIG. 2. Average concentration (\bullet , \circlearrowleft), average resistivity (\blacksquare , \Box), and contact resistance (\blacktriangle , \bigtriangleup), as a function of Si doping. (\bullet , \blacksquare , \blacktriangle) for As₄/Ga = (3-6), \circlearrowleft , \hookrightarrow) for As₄/Ga = 1-2).

face, as observed by the Reflection High Energy Electron Diffraction (RHEED) patterns shown in Fig. 1. At such high doping levels, As₄ flux had to be increased by a factor of at least 5 to maintain As stabilized surface and a good surface morphology. This phenomenon is not well understood at present, but it is certainly related to the accumulation of Si

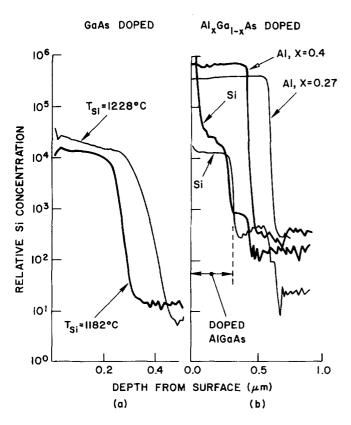


FIG. 3. SIMS results for (a) Si-doped GaAs, (b) Si-doped AlGaAs, for x = 0.27 and x = 0.4, with similar Si doping. Note that the accumulation is much more severe for x = 0.4. The enhancement of the Si signal in the undoped AlGaAs is due to an increase in yield of the SIMS detection.

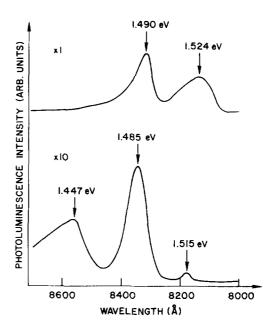


FIG. 4. (a) 6 K photoluminescence of 3×10^{18} cm⁻³ Si-doped GaAs. Although lineshape of the impurity band changes from sample to sample, the impurity band can be clearly identified. (b) 6 K photoluminescence of 2×10^{19} cm⁻³ Si-doped GaAs. The photoluminescence from impurity band disappears. The asymmetric lineshape of the 1.447-eV peak indicates the formation of donor-acceptor complexes.

on the surface. Figure 2 summarized the measured electron concentrations at room temperature (300 °K) by Hall effect using the van der Pauw method, for two different As₄/Ga flux ratios. For Si doping concentrations above 2×10^{19} cm⁻³, the surface morphology degrades after about 1000-Ă growth of GaAs independent of the As4 flux. The highest electron concentration of 1.1×10^{19} cm⁻³ was obtained for a Si doping concentration $N_{\rm Si}$ of 1.9×10^{19} cm⁻³ (at the cell temperature of 1200 °C). The lowest average resistivity of $5 \times 10^{-4} \Omega$ cm was obtained for a Si doping concentration of 3×10^{19} cm⁻³ (at a cell temperature of 1211 °C) suggesting nonhomogeneous doping. I-V characteristics of Schottky barriers formed by evaporating Au dots on the GaAs epilayers were also measured. The I-V curve was linear for N_{si} $\gtrsim 1.5 \times ^{19}$ cm⁻³ ($T_{\rm Si} > 1180$ °C) with the lowest resistance obtained for $N_{\rm Si} \sim 3 \times 10^{19} \, {\rm cm}^{-3}$ ($T_{\rm Si} = 1211 \, {\rm ^{\circ}C}$). Those results are also summarized in Fig. 2. We have checked by secondary ion mass spectroscopy (SIMS) the distribution of Si in the grown layers, and as shown in Fig. 3(a), Si accumulates towards the surface. Note that the Si concentration near the surface cannot be measured due to a much reduced SIMS sensitivity, however, one may assume that the Si concentration is much higher near the surface due to the absence of a SIMS signal dip, as supported by the contact measurements. In these samples, a mild etch of the surface [removing (100-200)Å] degrades considerably the contact resistance. Low temperature (6 K) photoluminescence (PL) measurements were also performed to characterize the heavily Sidoped materials. For Si impurity level below $\sim 1 \times 10^{19}$ cm⁻³, the PL results clearly show the formation of the impurity band although the line shape and peak position of the impurity band vary from sample to sample. The low energy side of the impurity band in Fig. 4(a) $(N_{\rm Si} = 3 \times 10^{18} {\rm cm}^{-3})$

would correspond to transitions from the bottom of the donor band to shallow acceptor levels. The high energy side of the impurity band would correspond to transitions from the Fermi level above the conduction band to the top of valence band. However, the PL due to impurity band disappears when the Si impurity concentration is above $\sim 1.5 \times 10^{19}$ cm⁻³. In Fig. 4(b) where $N_{\rm Si} = 2 \times 10^{19}$ cm⁻³, except the weak bound exciton peak at 1.515 eV produced by the buffer layer, and the Si acceptor free to bound transition at 1.485 eV, the most prominent luminescence is the peak at 1.447 eV. The broad asymmetric line shape suggests the formation of donor-acceptor complexes. The weaker PL intensity of the heavily doped samples is most likely due to the increased nonradiative recombination associated with Si precipitates and other defects cause by heavy doping. From the PL results, we believe that the formation of donor-acceptor complexes limits the practical electron concentration to $\sim 1 \times 10^{19} \text{ cm}^{-3}$.

Heavy doping of AlGaAs with Al mole fraction of about 30% was also attempted. For a growth rate of 1400 Å/h, substrate temperature of 600 °C and $T_{\rm Si}$ exceeding 1150 °C, an excess As₄ was necessary (As₄/Ga~2) to maintain an As-stabilized surface, although not as high as needed for the heavily doped GaAs. The previously established limit of Si-doped AlGaAs was ~ 3×10^{18} cm^{-3.7} We did not achieve average free electron concentration higher than the

reported value, however the surface Si concentration was very high, and increased with the Al mole fraction, causing a linear I-V characteristic of the Schottky barrier. (Contact resistance for $T_{\rm Si} \simeq 1180$ °C was ~ 6 and 1.7Ω cm² for As₄/Ga = 1 and 10, respectively). SIMS measurments revealed a significant accumulation of Si near the surface, for two Al mole fractions, as shown in Fig. 3(b).

In conclusion, we have studied heavily Si-doped GaAs and AlGaAs grown by MBE. The highest electron concentration obtained for GaAs was 1.1×10^{19} cm⁻³, which is higher than the previously reported limit of 5×10^{18} cm⁻³. SIMS results indicated Si accumulation near the surface. The Si Accumulation occurred more readily in AlGaAs than in GaAs. Our results suggest that Si could be a potentially useful *n*-type dopant for heavy doping, but probably not heavy enough for nonalloyed ohmic contacts with high barrier height.

¹P. A. Barnes and A. Y. Cho, Appl. Phys. Lett. 33, 651 (1978).

²W. T. Tsang, Appl. Phys. Lett. 33, 1022 (1978).

³C. E. C. Wood and B. A. Joyce, J. App. Phys. 49, 4854 (1978).

⁴J. J. Harris, B. A. Joyce, J. P. Gowers, and J. H. Neave, Appl. Phys. A28, 63 (1982).

⁵Y.G. Chai, R. Chow, and C. E. C. Wood, Appl. Phys. Lett. **39**, 800 (1981). ⁶M. Heiblum, E. Mendez, and L. Osterling (unpublished).

⁷T. J Drummond, W. G. Lyons, R. Fisher, R. E. Thorne, H. Morkoç, C. G. Hopkins, and C. A. Evans, Jr., J. Vac. Sci. Technol. 21, 957 (1982).