Secondary-ion mass spectrometry on δ-doped GaAs grown by molecular beam epitaxy

E. F. Schubert, H. S. Luftman, R. F. Kopf, R. L. Headrick, and J. M. Kuo
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

Improved resolution of secondary-ion mass spectrometry (SIMS) is obtained on Be δ-doped GaAs grown by molecular beam epitaxy at a temperature of 500 °C. The measured impurity distribution width is 29 Å, which corresponds to a SIMS resolution of $\Delta z_R = 25$ Å. Impurity diffusion lengths of $\leqslant 10$ Å can be detected by the technique. The surface segregation of Si impurities in δ-doped GaAs grown at 660 °C is investigated as a function of doping density. The segregation length increases with the Si density and is consistent with a segregation model based on the pinning of the Fermi level at the growing GaAs surface.

Spatial localization of one-dimensional impurity distributions along the epitaxial growth direction can be achieved by the δ-doping technique.[1] The technique allows one to generate narrow impurity distributions confined to one or a few lattice planes of a semiconductor. The impurity distribution can be considered as δ-function-like if the width of the doping distribution is much smaller than the spatial extent of the ground-state wave function of the free-carrier system.[1]

Several research groups employed secondary-ion mass spectrometry (SIMS) to assess the spatial localization of impurities in δ-doped III-V compound semiconductors[1-7] as well as for column IV semiconductors.[8,9] Despite the qualitative agreement that low growth temperatures are required to achieve the spatial localization of impurities, different conclusions were drawn from SIMS measurements on Si δ-doped GaAs grown under comparable conditions. It was suggested that significant Si dopant spread occurs during growth at normal molecular beam epitaxy (MBE) temperatures such as 550 °C,[5] while other groups found no evidence for spread at temperatures of 500–550 °C.[1,6] The present results resolve this discrepancy since we consider the concentration dependence of the Si impurity segregation.

In this letter we report on SIMS measurements with improved resolution on Be and Si δ-doped GaAs grown by MBE. A SIMS resolution of $\Delta z = 25$ Å is obtained which is sufficient to detect impurity diffusion lengths of $\leqslant 10$ Å. The superior resolution is obtained by optimized measurement and crystal growth conditions and an optimized structure. Furthermore, the segregation of Si impurities during growth at 660 °C is investigated. The segregation length is found to increase at higher Si doping density.

The epitaxial GaAs films are grown by molecular beam epitaxy (MBE) on semi-insulating ⟨001⟩ oriented GaAs substrates. The Varian Gen II growth system has an improved doping homogeneity due to an increased distance between the Si and Be Knudsen cells and the 2″ In-free mounted substrates. The layer sequence of the Be-doped sample consists of a 3000 Å GaAs buffer layer grown for smoothing purposes, one molecular monolayer of AlAs (2.83 Å), and a 1700-Å-thick GaAs top layer which contains two Be spikes of density $N_{\text{Be}}^{2D} = 5 \times 10^{12}$ cm^{-2} lo-

cated 200 and 700 Å below the epilayer surface. The layer sequence of the Si-doped samples consists of a 4000-Å-thick GaAs buffer layer, the Si-doping spike, and a 1000-Å-thick GaAs top layer. The areal Si doping density is varied between 1×10^{12} cm^{-2} and 1×10^{13} cm^{-2}. The Si-doped samples are grown at a high temperature of 660 °C in order to make segregation effects more pronounced. SIMS is measured on a Physical Electronics "PHI 6300" system. The primary-ion energy is varied between 1.0 and 3.0 keV. For Be- and Si-doped samples a O_2^+ and Cs^+ primary-ion beam is used, respectively. An angle of 60° incidence to the surface normal is used for sputtering to reduce the momentum transfer of sputtering primary ions along the growth direction. The raster area is of squared shape with an area of 750 μm × 750 μm. Gated detection is used for the secondary ions such that the secondary ions are detected from the central 9% of the rastered area. The full widths at half maxima of the SIMS profiles are determined by computer calculations directly from the spectra. The reproducibility of the width is better than 7% for identical sputtering and detection conditions. The depth scale of the SIMS measurements is calibrated by profiling the sputtered crater using a Dektak II profiler. The depth determined for the first Be spike is 194 Å ± 5%. Our MBE thickness calibration is known to be better than 5%, as concluded from optical reflectivity measurements on quarter-wave AlAs/GaAs multilayer reflectors. Thus, both depth calibrations are in agreement.

The SIMS profile of a Be δ-doped GaAs film is shown in Fig. 1. A narrow peak is observed at a depth of ~200 Å which corresponds to the Be δ-doped layer. The full width at half maximum of the Be peak is 29 Å, which is the narrowest SIMS profile measured for δ-doped GaAs grown at typical growth temperatures. From the symmetric shape of the profile, we conclude that surface roughness is the dominant broadening mechanism rather than the "knock-on" effect.

The resolution of the SIMS technique is generally obtained by assuming that the shape of the profile is a Gaussian distribution.[10] The symmetric Gaussian distribution is justified since the profile shown in Fig. 1 is symmetric. Provided that diffusion effects are negligible in the sample shown in Fig. 1 (which will be further demonstrated in the
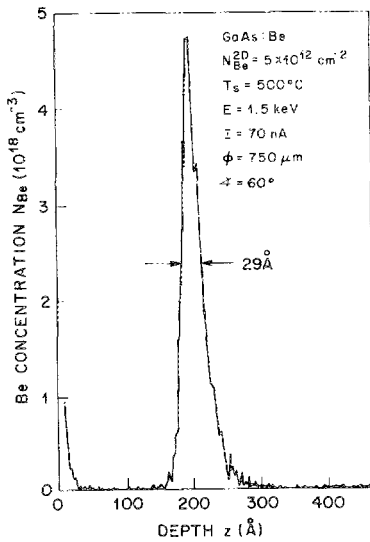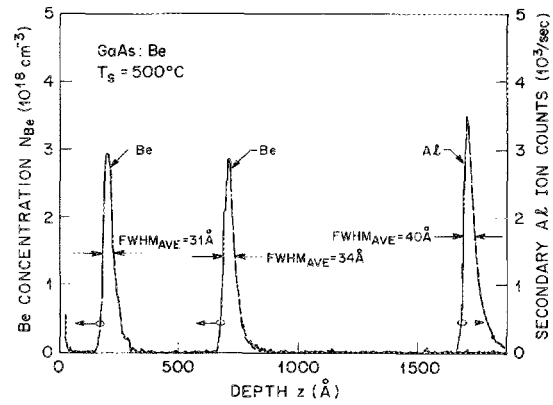
FIG. 2. Secondary-ion mass spectrometry profile on epitaxial GaAs with two Be δ-doped layers at 200 and 700 Å below the surface and on AlAs molecular monolayer at 1700 Å below the surface. The width of the peaks broadens linearly with sputtering depth.

FIG. 1. Secondary-ion mass spectrometry profile on epitaxial GaAs with a Be δ-doped layer 200 Å below the surface. The following parameters are used for the MBE growth and the measurement: Growth temperature 500 °C, primary-ion acceleration energy 1.5 keV, primary-ion current 70 nA, raster diameter 750 μm, sputtering angle 60°.

remainder of the letter), the profile shown is given by the resolution function of the technique. The resolution of the technique, Δz_R, is defined as twice the standard deviation of the Gaussian distribution,[10] i.e., $\Delta z_R = 2\sigma_r$. Since the full width at half maximum is 2.36 times larger than the standard deviation of a Gaussian distribution, the resolution of our measurement under optimized conditions is $\Delta z_R = 25$ Å. The reproducibility of measurements with this resolution is good, i.e., spectra measured under identical conditions on the same sample have a width of 29 Å ± 2 Å.

If impurities diffused out of the δ-doped plane, the measured SIMS profiles broaden as well. Assuming that the impurity profiles are of Gaussian shape the measured width of the SIMS profile is exactly given by

$$\Delta z_M^2 = \Delta z_D^2 + \Delta z_R^2, \qquad (1)$$

where $\Delta z_D = 2\sigma_D$ is the width of the impurity profile after diffusion. The resolution $\Delta z_R = 25$ Å and its reproducibility (± 7%) are known. Therefore we can determine the smallest impurity distribution width, i.e., diffusion length which can be determined by the technique. As an example we choose a diffusion length for impurities of $\Delta z_D / 2 = \sigma_D = \sqrt{2D\tau} = 10$ Å and obtain from Eq. (1) $z_M = 32$ Å which corresponds to a FWHM = 38 Å which represents a significant broadening of the profile as compared to the profile shown in Fig. 1 and can be easily detected. Thus, diffusion lengths of ≪10 Å can be clearly detected in our samples for the present optimized measurement conditions. This demonstrates that SIMS is the most sensitive structural method to determine impurity diffusion lengths in semiconductors.

The change of the resolution width with sputtering depth is shown in Fig. 2 . The spectra show two Be peaks

at a sputtering depth of 200 and 700 Å as well as a molecular monolayer of AlAs at a sputtering depth of 1700 Å. The widths of the peaks shown in Fig. 2 are average values obtained from four measurements with primary-ion energies of 1.0 to 1.5 keV and for raster areas ranging from 350×350 μm^2 to 750×750 μm^2. The average width of the first Be spike is 31 Å and increases to 40 Å for the Al spike.

It is reasonable to assume that the Al atoms represented by the third spike in Fig. 2 are contained within at most three atomic cation planes of the GaAs lattice. First, the Al-Ga interdiffusion coefficient is extremely small (≪10^{-28} cm^2/s) at 500 °C and has a high activation energy of 6 eV.[11] Second, high-resolution transmission electron microscopy studies on (AlGa)As/GaAs interfaces have not revealed diffusion of cations across the interface.[12]

The depth dependence of the SIMS resolution is usually expressed by the linear equation[10]

$$\Delta z_R = \alpha + \beta z, \qquad (2)$$

where α is the resolution for $z = 0$ and β is a parameter which represents the deterioration of the resolution with depth. The deterioration of depth resolution increases with sputtering depth because of the roughening of the crater surface due to the statistical nature of the sputtering process. The parameter β is obtained from the broadening of the first two Be peaks and has a value of $\beta = 0.005 = 0.5\%$. Note that this value is between the β values reported previously on δ-doped semiconductors.[5,6] The parameter α is determined (using $\beta = 0.5\%$) to be 24 Å for the previously mentioned optimized conditions, and is determined to be 26 Å for the average values shown in Fig. 2. Extrapolation of the SIMS resolution to a depth of 1700 Å yields a profile width of 41 Å ($\Delta z_R = 35$ Å), which is in agreement with the measured value of 42 Å ($\Delta z_R = 36$ Å). The consistency in the broadening behavior of the three peaks with depth can only be explained if diffusion effects of Be are negligible, i.e., the SIMS profiles are the resolution function of the instrument. Note that Si is known to be a slower diffusant in GaAs as compared to
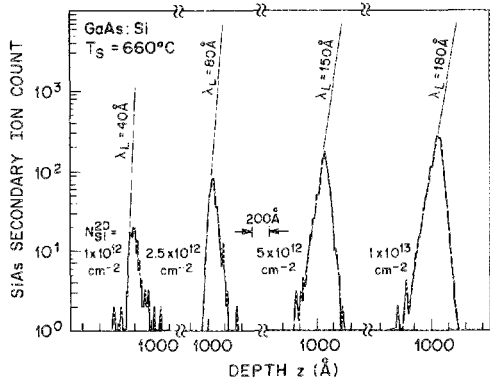
FIG. 3. Secondary-ion mass spectrometry profile on four Si δ-doped GaAs samples grown by MBE at 660 °C. The leading slope of the profiles is evaluated in terms of a length λ_L, within which the secondary-ion count decreases by a factor of 10. (100 ion counts corresponds to a concentration of 3×10^{18} cm^{-3}.)

FIG. 4. Segregation length λ_L as a function of Si density in δ-doped GaAs grown at 660 °C. The segregation length increases sublinearly with Si density.

Be.[13,14] Therefore, the present experiments confirm the irrelevance of diffusion effects for Be and Si in GaAs at MBE growth temperatures of 500–550 °C.

The picture of spatial localization of impurities changes at high growth temperatures where diffusion effects are larger.[13,14] In addition to diffusion, segregation effects were found in Si-doped[2,3,6] and Be-doped[2] GaAs. Schubert et al.[2] explained several segregation experiments by a model based on the pinning of the Fermi level at the growing semiconductor surface.[2] Impurities lower their energy by drifting towards the pinned surface. Beall et al.[7] developed a phenomenological model to quantitatively simulate the segregation process. The basis of their model is a rate equation which includes an impurity arrival rate, an incorporation rate, and a desorption rate.

The SIMS profiles of four Si δ-doped GaAs samples with different Si densities are shown in Fig. 3 . The profiles are measured at 3 kV primary-ion acceleration potential. The Si densities range between 1×10^{12} and 1×10^{13} cm^{-2}. The growth temperature of 660 °C is unusually high for the MBE growth of GaAs. However, segregation effects are more prominent at such high temperatures. The SIMS spectra are skewed towards the surface which indicates surface segregation. The segregation is especially pronounced at the highest Si densities. We evaluate the segregation quantitatively by defining a segregation length of the leading slope of the SIMS spectra, λ_L, in which the secondary-ion signal decreases by one order of magnitude. The trailing slope of the SIMS profiles is on the order of $\lambda_T = 90$ Å per decade of the secondary-ion count. The trailing slope remains approximately constant for the four samples. (For the lower primary-ion energy of 1.5 keV used in Fig. 1 we obtain $\lambda_T = 40$ Å.) Note that λ_T is partly determined by the "knock-on" effect by which primary sputtering ions transfer their momentum elastically to impurities which are then "implanted" deeper into the crystal. Both λ_L and λ_T are broadened due to the SIMS-induced "cascade mixing" effect and due to conventional diffusion.

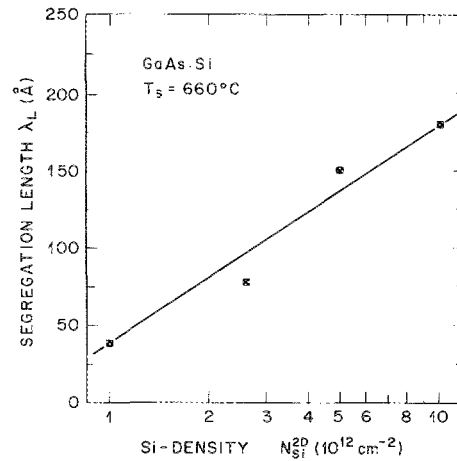The increase of the segregation length with impurity

density is shown in Fig. 4. The segregation length increases from $\lambda_L = 40$ Å for the lightly Si-doped sample to $\lambda_L = 180$ Å for the heavily Si-doped sample. The trend to segregation is obviously proportional to the density of Si impurities. Note that the results are not compatible with a solubility-limited incorporation of Si which would predict a top-hat distribution of Si. The increasing segregation length is consistent with the segregation model based on Fermi level pinning.[2]

In conclusion, secondary-ion mass spectrometry with improved resolution was employed for the analysis of Be and Si δ-doped GaAs grown by molecular beam epitaxy under MBE-typical growth conditions. An excellent SIMS resolution of $\Delta z_R = 25$ Å is obtained on Be-doped samples grown at 500 °C. The resolution allows one to detect diffusion lengths of $\leqslant 10$ Å. The surface segregation of Si in δ-doped GaAs is investigated as a function of Si density. The Si segregation length increases with the Si density.

[1] For a recent review, see E. F. Schubert, J. Vac. Sci. Technol. A 8, 2980 (1990).
[2] E. F. Schubert, J. M. Kuo, R. F. Kopf, A. S. Jordan, H. S. Luftman, and L. C. Hopkins, Phys. Rev. B 42, 1364 (1990).
[3] R. B. Beall, J. B. Clegg, and J. J. Harris, Semicond. Sci. Technol. 3, 612 (1988).
[4] R. B. Beall, J. J. Harris, J. B. Clegg, J. P. Gowers, B. A. Joyce, J. Castagné, and V. Welch, in GaAs and Related Compounds 1988, Inst. Phys. Conf. Ser. 96, 17 (1989).
[5] J. B. Clegg and R. B. Beall, Surf. Interface Anal. 14, 307 (1989).
[6] A.-M. Lanzillotto, M. Santos, and M. Shayegan, Appl. Phys. Lett. 55, 1445 (1989).
[7] R. B. Beall, J. B. Clegg, J. Castagné, and J. J. Harris, Semicond. Sci. Technol. (to be published).
[8] R. L. Headrick, A. F. J. Levi, H. S. Luftman, J. Kovalchick, and L. C. Feldman (unpublished).
[9] H. Jorke, H. Kibbel, F. Schäffler, A. Casel, H.-J. Herzog, and E. Kasper, Appl. Phys. Lett. 54, 819 (1989).
[10] A. Benninghoven, F. G. Rüdenauer, and H. W. Werner, in Secondary Ion Mass Spectrometry (Wiley, New York, 1987), pp. 900–910.
[11] T. Y. Tan and U. Gösele, Appl. Phys. Lett. 52, 1240 (1988).
[12] J. M. Gibson (private communication, 1990).
[13] E. F. Schubert, J. B. Stark, T. H. Chiu, and B. Tell, Appl. Phys. Lett. 53, 293 (1988).
[14] E. F. Schubert, J. M. Kuo, R. F. Kopf, H. S. Luftman, L. C. Hopkins, and N. J. Sauer, J. Appl. Phys. 67, 1969 (1990).