H2Se DOPING OF MOCVD GROWN GaAs AND GaAlAs
R. Glew

To cite this version:

HAL Id: jpa-00222253
https://hal.archives-ouvertes.fr/jpa-00222253
Submitted on 1 Jan 1982

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
H₂Se DOPING OF MOCVD GROWN GaAs AND GaAlAs

R.W. Glew

The General Electric Company, p.l.c., Hirst Research Centre, Wembley, England

Abstract.- In the growth of epitaxial layers of GaAs and GaAlAs by the MOCVD process a superlinear relationship between the n-type doping and the H₂Se mole fraction in the gas phase has been found. This superlinear effect has been observed both with atmospheric and reduced pressure depositions. The anomalous doping effect is compared to H₂S doping where a linear doping relationship has been observed. The dopant incorporation mechanism for sulphur and selenium are different and the possible growth mechanisms are discussed.

Introduction - It has been generally assumed in epitaxial growth on GaAs substrates that there is a linear dependence of the electron concentration with the dopant mole fraction (1). However in a recent comparison of H₂S and H₂Se doping of GaAs by the MOCVD method (2), while a linear relationship between the H₂S mole fraction in the gas phase and the doping was found, for H₂Se the doping relationship was superlinear. This anomalous doping behaviour was observed for atmospheric pressure depositions. Further experiments with H₂Se doping of GaAs and GaAlAs at reduced pressure have been performed. In this paper the growth conditions for superlinearity are given and the dopant incorporation mechanisms are investigated.

Experimental - Epitaxial layers were grown by the MOCVD technique in a Crystal Specialties 421 reactor. The 8 cm diameter process tube is shown in Figure 1. The substrates were mounted on a coated graphite susceptor perpendicular to the incoming gas flow. The chromium doped substrates, oriented 2° off the (100) axis, were cleaned and then etched in a (3 H₂SO₄ : 1 H₂O₂ : 1 H₂O) solution prior to loading. Electronic grade sources were used. The TMG and TMA were obtained from Alpha Ventron and Texas Alkyls; the 10% arsine in hydrogen from Air Products and the 50 ppm H₂Se in hydrogen from British Oxygen Company.

Several hydrogen selenide sources were used in this investigation. Total flow rates were approximately 1 L/min for atmospheric pressure depositions and 5 L/min for reduced pressures (75 Torr). Epitaxial layer uniformity and surface quality was good. Undoped layers were typically 2 x 10¹⁵ cm⁻² with a room temperature mobility of 6,500 cm²/Vs. Room temperature doping levels were obtained from a Miller feedback profiler and an electrochemical profile plotter. Hall mobility measurements were obtained from van der Pauw measurements. Epilayer thicknesses in this investigation were in the range 1 to 2 μm; thicknesses were taken from the electrochemical profiler and checked by a staining technique. Aluminium concentrations were measured by an X-ray multiple diffraction technique.
Fig 1: MOCVD reactor tube

Results and discussion - For H₂Se doping of GaAs at atmospheric pressure (Figure 2) the doping increases with the dopant mole fraction with the relationship: \( n \propto (H₂Se \text{ m.f.})^{3/2} \). This has been shown for a temperature range of 650°C to 800°C. Similar

![Diagram of MOCVD reactor tube]

Fig 2: Plot of electron concentration with dopant mole fraction for H₂Se and H₂S doping of GaAs

Selenium doping superlinearities have been observed for different As/Ga ratios and for growth on n⁺ substrates (both Si and Te doped). For comparison, in Figure 2, the previously reported (2) linear doping relationship for sulphur is shown. At a doping level of 10¹⁸ cm⁻³ the selenium is about 10 times more efficient at doping than sulphur whereas Mori et al (3) found it about 100 times more efficient. Comparing the results of Mori et al (3) and Figure 2 it is seen that the selenium is less efficient and the sulphur is more efficient than in the work of Mori et al (3).
The superlinear relationship has also been found for growth at reduced pressure (Figure 3) for temperatures of 700 and 775°C. Here the relationship: \( n \propto (H_2Se \text{ m.f.})^{1.4} \) is observed. The electron concentrations at 75 Torr is lower than that at 760 Torr for the same \( H_2Se \) concentration because of the different As/Ga ratios and pressures. The doping is inversely proportional to the As/Ga ratio (2), and higher As/Ga ratios are required for low pressure depositions so as to retain good properties. In the case of \( H_2Se \) doping of GaAs at reduced pressure (Figure 4) the superlinear relationship is: \( n \propto (H_2Se \text{ m.f.})^{2.6} \). (The aluminium composition was 0.23 ± 0.01 for the layers). The doping superlinearity is increased with the addition of TMA to the gas stream. For GaAlAs the electron mobility decreased from 1,200 cm²/Vs at \( 9.5 \times 10^{16} \) cm⁻³ to 490 cm²/Vs at \( 1.7 \times 10^{18} \) cm⁻³. These doping superlinearities can be advantageous as a large range of doping levels are obtained from a single flow controller.

![Fig 3: Plot of electron concentration with \( H_2Se \) mole fraction for low pressure deposition of GaAs](image1)

![Fig 4: Plot of electron concentration with \( H_2Se \) mole fraction for low pressure deposition of GaAlAs](image2)

Superlinear doping behaviour has been reported previously, but explanations were not given. In the growth of GaAs by the \( AsCl_3 \) method Sankaran (4) has observed superlinearity when doping with Te. Taylor (5) observed similar effects when doping GaP with selenium on the (111)B face. In the MOCVD system it has been observed by Hallais et al (6) when doping GaAs with \( H_2Se \), Ludowise et al (7) when doping GaInAs with \( H_2Se \) and Lewis et al (8) when doping GaAs p-type with Mg. These results are in direct contradiction to those of Andre et al (9) and Mori et al (3) who have shown linear relationships for selenium doped GaAs and GaAlAs. The reason why selenium superlinearity is always observed by some workers (2,7) sometimes by others (5,6,10) and never by others (3,9) is unknown. But of particular interest are the results of Hollan et al (10) where, in the \( AsCl_3 \) system, superlinear behaviour was shown for \( H_2Se \) (despite experimental difficulties) and linear for selenium vapour. This shows that the dopant incorporation mechanism for selenium can depend on what form the dopant is introduced to the reactor. The reactor geometry, mixing conditions, stagnant layer properties and flow dynamics are important parameters in the dopant incorporation mechanism and it is these which are unknown in the growth process. Previously (2) it was proposed that there was a parasitic gas phase reaction above the susceptor which gave rise to the superlinear behaviour. This is now known not to be the case because superlinear behaviour occurs at reduced pressure growth where
parasitic reactions are significantly reduced (11). It has been assumed that there is a linear relationship between the impurity incorporation and the electron concentration obtained. This is known to be true for sulphur (1) and tin (12) doping but not for selenium. Further work, including SIMS analysis of grown layers will be performed.

In Figure 5 the variation of electron mobility with electron concentration of $H_2Se$ and $H_2S$ are compared. Above $6 \times 10^{17}$ cm$^{-3}$ the selenium doped layers have the higher mobilities and the sulphur doped layers are higher for dopings of less than $6 \times 10^{17}$ cm$^{-3}$. The results are similar to those of Hollan et al (10) where higher values were observed for selenium doped layers for values of $n$ greater than $4 \times 10^{17}$ cm$^{-3}$. From these mobility values the compensation ratio (defined as $\theta = \frac{N_A}{N_D}$) at room temperature can be found by use of the table of Walukiewicz et al (13). The plot of compensation ratio against doping for $H_2S$ and $H_2Se$ is shown in Figure 6. The sulphur doping compensation ratio is constant and then increases as the layer becomes

---

**Fig 5**: Plot of room temperature electron mobility with electron concentration for $H_2Se$ and $H_2S$ doped layers

**Fig 6**: Plot of compensation ratio with electron concentration for $H_2Se$ and $H_2S$ doped layers
saturated, whereas the selenium compensation ratio decreases for increasing dopant. Therefore the dopant incorporation mechanism for sulphur and selenium are quite different. Both sulphur and selenium sit on similar lattice sites because the doping has been found to be inversely proportional to the As/Ga ratio (2).

In Figure 7 the variation in growth rate with dopant (at constant temperature, As/Ga ratio and TMG concentrations) is shown. For selenium the growth rate increases slightly whereas for sulphur a much larger increase in growth rate is measured. The thickness control of sulphur doped layers is therefore harder than for selenium. Growth rate changes have been observed before for GaAs (14) but in that case the growth rate decreased with an increase in the n-type dopant (Te). Several dopant influencing mechanisms have been proposed and are discussed by Pogge (14). On the growing surface the sulphur could either increase the number of growth sites or change the surface charge and therefore increase the growth rate.

![Graph showing growth rate with dopant mole fraction for H₂Se and H₂S doped layers grown at 720°C under constant TMG concentration and As/Ga ratio.](image)

**Fig 7**: Plot of growth rate with dopant mole fraction for H₂Se and H₂S doped layers grown at 720°C under constant TMG concentration and As/Ga ratio.

Heat treatment (at 800°C) of GaAs:Se layers showed a reduction in the carrier concentration for layers doped over 3 x 10¹⁸ cm⁻³, similar to the results of Hollan et al (10). The surface solubility of selenium during growth is higher than the bulk value. The maximum doping from vapour phase growth is ~10¹⁹ cm⁻³ while the maximum bulk doping is ~3 x 10¹⁸ cm⁻³. During heat treatment Ga₂Se₃ precipitates are thought to form in the epitaxial layers and so reduce the effective electron concentration.

The growth rates used in this investigation were ~0.1 μm/min and kinetic controlled growth processes take place. The conditions for kinetic growth (15) is that the growth velocity, $v > D \lambda$ where D is the diffusivity and $\lambda$ the reciprocal intrinsic Debye length. At 750°C $D \lambda$ for selenium is ~6 x 10¹² cm/s and ~6 x 10⁻⁸ cm/s for sulphur (both less than the growth velocity). The theory of dopant incorporation (1) which predicts a linear doping relationship from thermodynamic equilibrium considerations is therefore not applicable. Doping superlinearity occurs in the vapour phase growth for dopants, such as selenium and tellurium, which have slow diffusivities (~2 x 10⁻¹⁷ cm²/s and ~10⁻¹⁸ cm²/s at 750°C respectively), whereas for other dopants, such as sulphur, with a far higher diffusivity (2 x 10⁻¹³ cm²/s at 750°C) the doping is linear.

The dopant incorporation can be thought to be due to the non-equilibrium absorption of the dopants at the growing surface followed by trapping as the layer grows, previously proposed by Mullen (16). Selenium is much more efficiently incorporated
into the lattice than sulphur. At high doping levels ($>3 \times 10^{18}$ cm$^{-3}$) the selenium is artifically frozen into the GaAs growing lattice because of its low diffusivity. On heat treatment the selenium moves so as to reduce the electron concentration whereas sulphur which has a higher diffusivity performs this annealing stage during growth. Mullin (16) has pointed out that little is known about elemental incorporation during vapour growth so that a true understanding of the superlinear doping is not forthcoming.

Conclusions - Doping superlinearity has been found for H$_2$Se doping in GaAs and GaAlAs both for atmospheric and low pressure growth. The growth process is kinetic and hence the thermodynamic model which predicts a linear doping relation is no longer valid. The superlinearity is not due to a parasitic gas phase reaction because the effect is still observed under low pressure conditions. The effect occurs for slow diffusing elements such as selenium and tellurium, which are efficient dopants, but not for fast diffusing ones like sulphur, which are less efficient dopants. The growth rate is fast so that the selenium concentration at the surface is frozen into the growing lattice so that very high concentrations are produced which can be reduced by annealing. It has also been found that the injection of H$_2$S into the reactor produces an increase in the growth rate whilst this does not occur for H$_2$Se doping. The growth mechanisms for sulphur and selenium are therefore different. A satisfactory model for dopant incorporation cannot be given because there are too many unknown parameters in the growth process.

References -

2. GLEW R.W., Int Symp on GaAs and Related Compounds, Japan 1981 (Inst Phys Conf Ser No 63), p 581
4. SANKARAN R., J Cryst Growth, 50, (1980), 859
8. LEWIS C.R., DIETZE W.T., LUDOWISE M.J., Electronics Letters, 18, (1982), 569
16. MULLIN J.B., J Crystal Growth, 42, (1977), 77