DIFFUSION OF NOBLE METALS, Zn AND Ge IN GaSb SINGLE CRYSTALS

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Abstract

Diffusion of Cu, Ag, Au, Ge and Zn in single crystal gallium antimonide has been carried out by measuring Hall effect according to van der Pauw, conductivity, energy dispersive X-ray (EDX) and surface electron microscopy. The best results have been obtained in excess of antimony. The resulting diffusion data in GaSb are diffusivity D_o, activation enthalpy Q, carrier density p and mobility μ at 300 K:

Ag: D_o=1.8·10^{-4} cm^2 s^{-1}, Q=1.2 eV, p=6·10^{18} cm^{-3}, μ=550 cm^2 (Vs)$^{-1}$,
Au: D_o=6.6·10^{+3} cm^2 s^{-1}, Q=2.7 eV, p=5·10^{18} cm^{-3}, μ=500 cm^2 (Vs)$^{-1}$,
Cu: D_o=3.2·10^{+8} cm^2 s^{-1}, Q=2.7 eV, p=2·10^{18} cm^{-3}, μ=150 cm^2 (Vs)$^{-1}$,
Zn: D_o=9.2·10^{-2} cm^2 s^{-1}, Q=1.8 eV, p=2·10^{20} cm^{-3}, μ= 80 cm^2 (Vs)$^{-1}$,
Ge: D_o=1.0·10^{-1} cm^2 s^{-1}, Q=1.7 eV, p=1·10^{19} cm^{-3}, μ=320 cm^2 (Vs)$^{-1}$.

Keywords: diffusion, noble metals, single crystals

Introduction

Gallium antimonide is a p-type III-V semiconductor with a narrow band gap of E_g=812 meV. It is applied in high speed opto-electronic devices, for long wavelength detectors ($\lambda \geq 1.5$ μm) and IR laser diodes [1]. High quality GaSb substrates with definite types of impurities and free carrier concentration in addition to low level dislocation densities are required for the epitaxial growth of these diodes. Self-diffusion and diffusion of zinc in GaSb have been investigated [2–6]. Zn is the most examined doping material in GaSb. Diffusion of Zn in GaSb has been first reported by Kyuregyan and Stuchebnikov [3]. They obtained smooth diffusion profiles which cannot be described by a complementary error function. They summarized that the diffusivity is proportional to Zn concentration, c_{Zn}, for diffusion below T=600°C and that the diffusion coefficient varies as c_{Zn}^2 for diffusion above T=600°C. Sundaram and Gruenbaum [4] have measured profiles with kinks, indicating similar diffusion mechanisms of Zn in GaSb and

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in GaAs. They evaluated concentration dependent diffusion coefficients using the Boltzman-Montano analysis. According to Kagawa and Motosugi [5] Zn diffusion in GaSb occurs by a conventional vacancy model. Little is known about other dopants or metals, that may serve as contact materials. The aim of this work was to obtain *p*-type and *n*-type GaSb material by diffusion of different dopants and to determine the properties of these dopants by the four-point probe method as well as by measuring conductivity and Hall-effect according to van der Pauw, EDX and surface electron microscopy.

Experimental results

Single crystals of gallium antimonide have been grown in the (111) direction by Czochralski technique without encapsulant in a flowing hydrogen atmosphere. A small amount of antimony (0.1 m%) was added into the melt to prevent the nonstoichiometric crystal growth due to the evaporation of antimony [7]. The residual defect concentration was $p=1.4\cdot10^{17}$ cm^{-3} with a Hall mobility of $\mu_p=$ 630 cm^2 (Vs)$^{-1}$ at $T=300$ K. Temperature dependent Hall-effect measurements revealed a shallow activation energy of $E_A=34$ meV above the valence band. This is the well-known first ionization state of a double ionizable acceptor in as grown GaSb [8, 9]. Diffusion profiles of copper, silver, gold, germanium and zinc have been obtained. The investigations include the determination of the following intrinsic and extrinsic properties: Hall conductivity and mobility, carrier type and concentration, diffusion constant, activation enthalpy, solubility, energy dispersive X-ray and surface electron microscopy. The EDX-analysis of selected samples confirmed the presence of diffusion material in the surface region. The diffusion data were obtained in the range $T=450$ to 680°C, the Hall data in the range $T=80$ to 380 K. All diffusion experiments have been carried out with excess of antimony. The results are summarized in the following chapter.

Diffusion data and discussion

The temperature dependent diffusion coefficients of all investigated dopants – with the exception of the element Zn – can be described very well by Arrhenius plots to determine the prefactors D_0 of the diffusion coefficients and the activation enthalpies Q.

Diffusion of Ag in GaSb has been carried out between 530 and 650°C. Two profiles are shown in Fig. 1. The data have been fitted by a complementary error function. The results for Ag diffusion in GaSb are shown in Figs 6–8: $D_0=1.8\cdot10^{-4}$ cm^2 s^{-1}, $Q=1.2$ eV, $p=6\cdot10^{18}$ cm^{-3}, $\mu=550$ cm^2 (Vs)$^{-1}$. No literature values have been available for Ag diffusion in GaSb. The data for silver indicate a substitutional mechanism by Gallium vacancies. Silver is expected to be a *p*-type dopant, as observed by Hall-effect. Diffusivity D_0 and activation

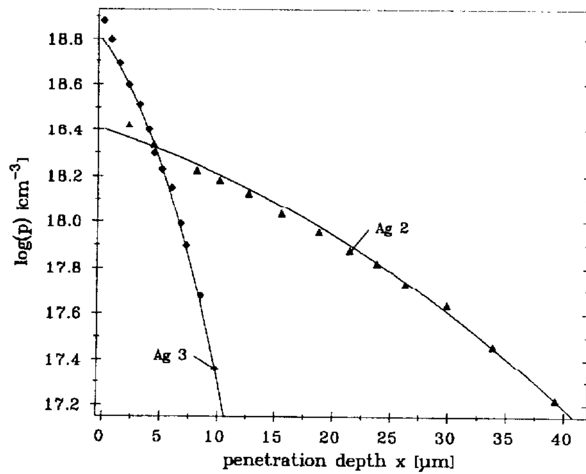

Fig. 1 Diffusion profiles of Ag in p-type GaSb: Hole concentration as a function of distance (Ag 2: T=600°C, t=18 h; Ag 3: T=650°C, t=2 h). The solid lines represent complementary error function fits to the experimental sheet conductance data

enthalpy Q, solubility and mobility support the model of a simple vacancy mechanism.

Diffusion profiles of Au in GaSb are shown in Fig. 2. The data have also been fitted by a complementary error function. The results for Au diffusion in GaSb are summarized in Figs 6–8: $D_o=6.6\cdot10^{+3}$ cm^2 s^{-1}, Q=2.7 eV, $p=5\cdot10^{18}$ cm^{-3} and μ=500 cm^2 (Vs)$^{-1}$. Again no literature values have been found for this diffusion.

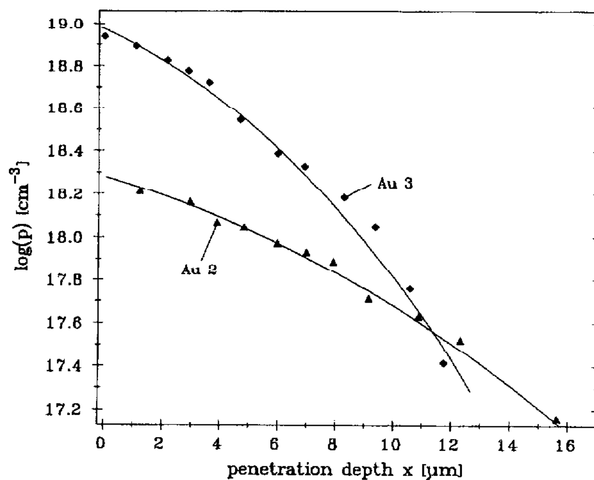

Fig. 2 Diffusion profiles of Au in p-type GaSb: Hole concentration as a function of distance (Au 2: T=680°C, t=4 h; Au 3: T=600°C, t=32 h). The solid lines represent complementary error function fits to the experimental sheet conductance data

Gold is very large and may not fit into a simple vacancy mechanism. The high values of diffusivity D_0 and activation enthalpy Q are similar to self-diffusion [6] and the same double vacancy diffusion mechanism should apply, which is suggested for self-diffusion in the literature [6, 8 and 9].

Diffusion profiles of Cu in GaSb are shown in Fig. 3. The data have also been fitted by a complementary error function. The results for Cu diffusion in GaSb

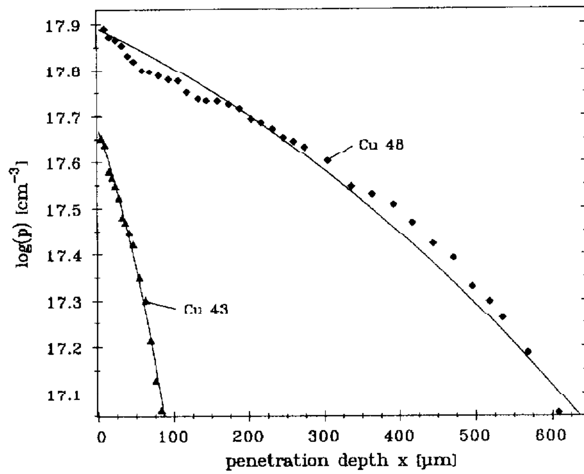

Fig. 3 Diffusion profiles of Cu in p-type GaSb: Hole concentration as a function of distance (Cu 43: T=500°C, t=14 h; Cu 48: T=650°C, t=0.75 h). The solid lines represent complementary error function fits to the experimental sheet conductance data

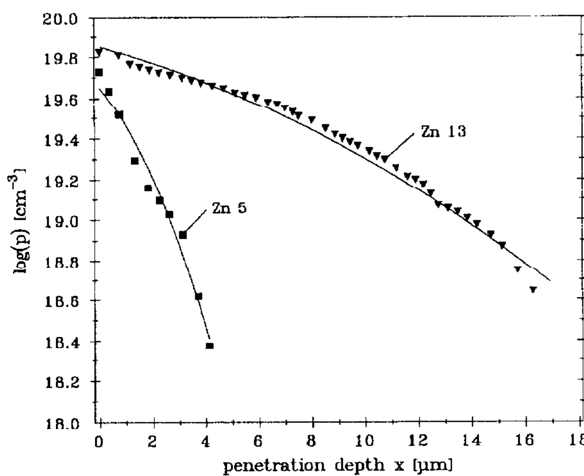

Fig. 4 Diffusion profiles of Zn in p-type GaSb: Hole concentration as a function of distance (Zn 5: T=560°C, t=6 h; Zn 13: T=640°C, t=12 h). The solid lines represent complementary error function fits to the experimental sheet conductance data

are summarized in Figs 6, 7 and 8: D_o=3.2·10^{+8} cm^2 s^{-1}, Q=2.7 eV, p=2 ·10^{18} cm^{-3} and μ=150 cm^2 (Vs)$^{-1}$. For Cu the high value D_o=3.2·10^{+8} cm^2 s^{-1} indicates an interstitial-substitutional diffusion mechanism for copper in gallium antimonide, which is often discussed for transition metals in GaAs [2]. The low mobility indicates a high defect concentration due to the copper doping and agrees with the

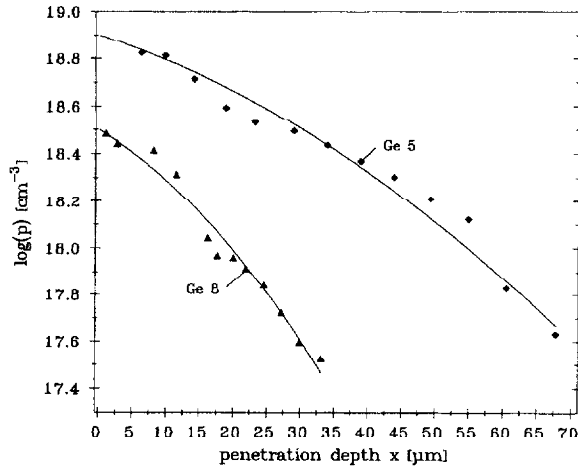

Fig. 5 Diffusion profiles of Ge in p-type GaSb: Hole concentration as a function of distance (Ge 5: T=620°C, t=45 h; Ge 8: T=580°C, t=48 h). The solid lines represent complementary error function fits to the experimental sheet conductance data

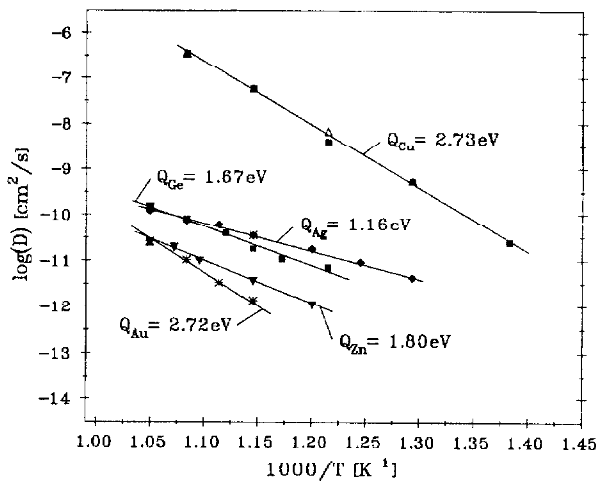

Fig. 6 Temperature-dependent diffusion coefficients (log$D$(1/T)) and activation enthalpies (Q) of several impurities in p-type GaSb, diffusion experiments are performed with presence of Sb. The solid lines are least square fits of experimental diffusion data

idea of the model, that interstitial copper may kick out Ga to jump to a substitutional site.

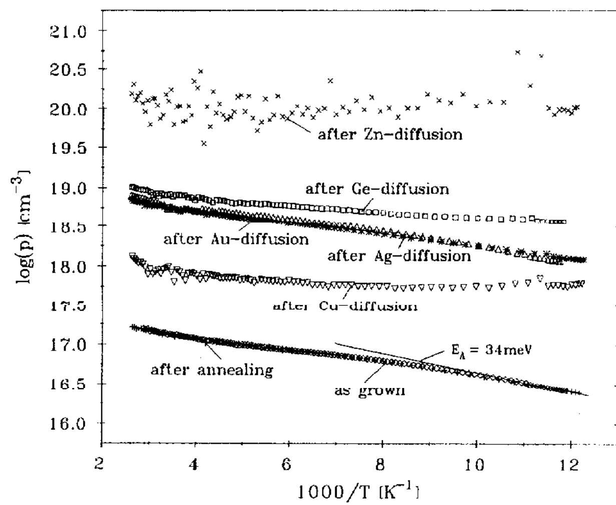

Fig. 7 Hole concentration in p-type GaSb as a function of 1/T from temperature-dependent Hall-effect measurements by means of the van der Pauw technique. The figure shows a comparison of a GaSb-sample as grown and a GaSb-sample after annealing (with Sb) at T=600°C respectively with GaSb-samples after diffusion (with Sb) of several dopants at T=650°C. A shallow acceptor activation energy of E_A=34 meV in p-GaSb (as grown) is shown too

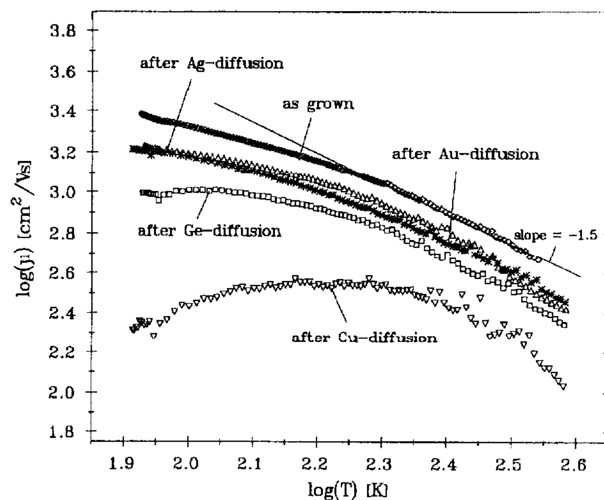

Fig. 8 Hole mobility in p-type GaSb as a function of $1/T$: A sample as grown is compared with samples after diffusion (with Sb) of several dopants at T=650°C. A van der Pauw geometry is used for temperature-dependent Hall-effect and conductivity measurements

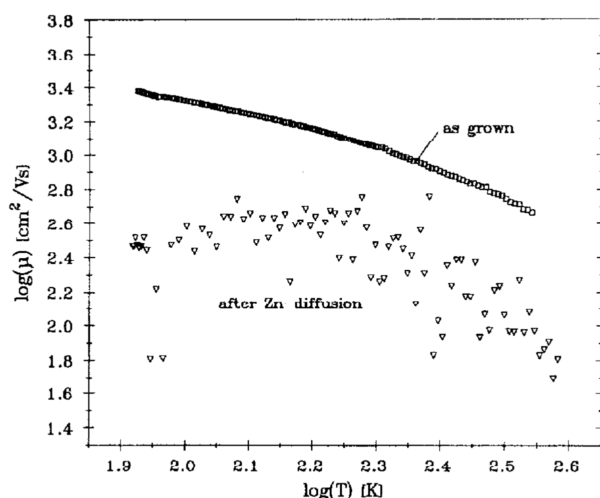

Fig. 9 Hole mobility after Zn-diffusion (with Sb) in p-type GaSb as a function of $1/T$ compared with a sample as grown. A van der Pauw geometry is used for temperature-dependent Hall-effect and conductivity measurements

Diffusion profiles of Zn in GaSb are shown in Fig. 4. The data have been compared to a complementary error function. The results for Zn diffusion in GaSb are summarized in Figs 6, 7 and 9: D_0=9.2·10^{-2} cm^2 s^{-1}, Q=1.8 eV, p=2·10^{20} cm^{-3}, μ=80 cm^2 (Vs)$^{-1}$. The data agree rather well with the literature [3, 5]. Zn shows a low diffusion enthalpy Q. According to EDX all Zn atoms are found on Ga sites. However, the scattering values of solubility p and the very low mobility indicate a substantial increase of defects. Electron microscopy shows an increase in surface defects, the profiles do not follow a complementary error function. This supports the idea, that Zn is solved in GaSb even at very high Zn concentrations by creating its own defects.

Diffusion profiles of Ge in GaSb are shown in Fig. 5. The data have also been fitted by a complementary error function. The results for Ge diffusion in GaSb are summarized in Figs 6, 7 and 8: D_0=1.0·10^{-1} cm^2 s^{-1}, Q=1.7 eV, p=1·10^{19} cm^{-3}, μ=320 cm^2 (Vs)$^{-1}$. Germanium may fit into Ga sites as a donor or into Sb sites as an acceptor. Since the covalent radius of Sb is larger than Ga, group IV atoms should tend to occupy Sb sites. Commonly, a group IV impurity in a III–V compound will occupy a lattice site which most closely matches its covalent radius, as this will minimize the lattice strain and the free energy of the crystal, respectively. The Hall data show p conductivity at high Ge concentrations, indicating that Ge will be, indeed, on Sb sites. The diffusion data D_0 and the activation enthalpy Q support a Sb vacancy mechanism for Ge in GaSb. The mobility is decreased by a factor of two after Ge diffusion.

Conclusions

So far we have obtained only informations about several *p*-type dopants in GaSb. However, we did not succeed in creating *n*-type GaSb by diffusion of the dopants Te and Se in sufficient high concentrations. Obviously, *n*-type GaSb can only be obtained by adding these dopants to the melt.

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