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Investigations of Extended Defects after Sulfur Diffusion in GaAs

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Abstract. We demonstrate that sulfur in-diffusion is a suitable tool to study the diffusion on the arsenic sublattice. The interaction of sulfur with dislocations and the formation of extended defects is investigated in detail by means of cathodoluminescence and transmission/analytical electron microscopy. The sulfur in-diffusion is governed by the kick-out mechanism. The diffusion proceeds for low sulfur concentrations under equilibrium conditions for As self-interstitials. In this case the diffusion profile is errorfunction-like and essentially determined by the sulfur diffusion coefficient. For higher sulfur concentration the sulfur diffuses under non-equilibrium conditions. Extended defects were formed during the in-diffusion process. They were observed up to a depth larger than the sulfur diffusion profile. The diffusion into dislocation-rich GaAs was investigated to study the interaction of sulfur with extended defects. An enrichment of sulfur at dislocations was found.

1 Introduction

Sulfur in-diffusion experiments in GaAs were performed to obtain information about diffusion properties of intrinsic lattice defects as well as the sulfur atoms themselves. There are a lot of data available for diffusion on the Ga sublattice in GaAs [1], because important dopants like Si, Zn, and Be are solved on this sublattice. Hence, this process is well understood. In the last years, there are also several new investigations on diffusion on the As sublattice [2, 3, 4, 5]. One technologically interesting point is that carbon, which is solved on the As sublattice, can be used as a slowly diffusing acceptor. There are also some new applications of sulfur as n-type dopant in transistor devices [6, 7]. Furthermore, the fabrication of electrically homogeneous GaAs wafers requires annealing steps after crystal growth [8, 9]. Arsenic diffusion and precipitation during annealing have to be considered to optimize these processes. Scholz et al. [4] pointed out that As self-diffusion is governed by the two interstitial-substitutional diffusion mechanisms, the kick-out mechanism and the Frank-Turnbull mechanism. The S in-diffusion is governed by the kick-out mechanism alone [10]. In this way, we can obtain information on the kick-out part of the As self-diffusion by studying S in-diffusion.

The interaction of point defects and extended defects is important because there are always dislocations in GaAs crystals. Studies on interaction of copper with dislocations show that the effects on the Ga sublattice depend on the diffusion properties of point defects [11]. It was found that the equilibrium concentrations of intrinsic point defects can be changed over a distance of up to several μm around dislocations. In the work presented here, we carried out similar experiments with S diffusion on the As sublattice.

2 Experiments

For sulfur in-diffusion experiments we used semi-insulating (SI) liquid-encapsulated Czochralski grown GaAs. The (001) surface was scratched with a microhardness indenter in [010] direction in order to generate fresh dislocations. The in-diffusion experiments were performed in sealed quartz ampoules after evacuating them to a pressure below 10^{-5} mbar. A solution of sulfur in benzene was added to the annealing ampoule. So we were able to provide a specific surface concentration of sulfur in our samples. An arsenic pressure of 1 bar during the annealing experiment was established by inserting metalic arsenic before sealing the ampoule. Annealing was carried out with various times and temperatures. The samples were either quenched in water or cooled down with a cooling rate of about 6 °C/min.

Undamaged samples were used to study S in-diffusion profiles, which were measured by secondary ion mass spectroscopy (SIMS). Cathodoluminescence (CL) spectroscopy and microscopy were performed with an OXFORD MonoCL system attached to a TESLA BS300 scanning electron microscope. A photomultiplier tube with a sensitivity range from 400 up to 900 nm and a germanium diode which is sensitive from 800 to 1600 nm were used as detectors. Transmission electron microscopy (TEM) was carried out with an analytical electron microscope (AEM) VACUUM GENERATORS HB501-UX, which is equipped with a KEVEX energy dispersive X-ray (EDX) detector. Additionally, we used a JEOL JEM1000 high-voltage transmission electron microscope.

3 In-diffusion profiles of sulfur in GaAs

The diffusion coefficients of S in GaAs given in the literature varies over several orders of magnitude [6, 12, 13, 14, 15]. For the comparison of the data, it has to be considered that not all the sulfur is electrically active in GaAs [10, 15]. Additionally, Fick's second law is only valid under certain conditions. As found by Uematsu et al. [10], the kick-out mechanism,

$$i_S \longleftrightarrow S_{As} + I_{As}, \tag{1}$$

can describe different sets of experimental data. i_S are sulfur atoms on interstitial sites, S_{As} sulfur atoms on As lattice sites, and I_{As} As self-interstitials. The in-diffusion profiles strongly depend on the boundary conditions, i.e. on the equilibrium concentration of i_S ($c_{i_S}^{eq}$) and S_{As} (c_S^{eq}) at the surface. One possibility to control the equilibrium concentration at the surface is

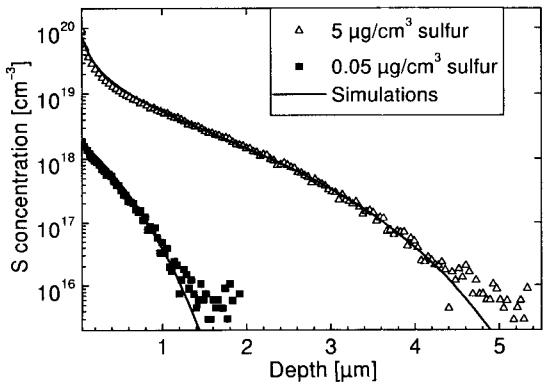


Fig. 1. Sulfur in-diffusion profiles measured by SIMS. The sample was annealed at 1100 °C for 7 min and different S concentrations in the gas phase (symbols).

to change the sulfur concentration in the gas phase over the GaAs sample. In Fig. 1, two S in-diffusion profiles are plotted after the same treatment but with different sulfur concentrations in the gas phase. The depth and the shape of the profiles change dramatically under these conditions. The reason is the change in $c_{i_S}^{eq}$ and the change in the related transport capacity $D_{i_S} c_{i_S}^{eq}$. If the transport capacity of i_S is smaller than or equal to the transport capacity of I_{As}, i.e. $D_{i_S} c_{i_S}^{eq} \leq D_{I_{As}} c_{I_{As}}^{eq}$, then the diffusion proceeds under equilibrium of intrinsic point defects. In this case, the I_{As} are quick enough that always $c_{I_{As}} = c_{I_{As}}^{eq}$. The effective diffusion coefficient is determined by

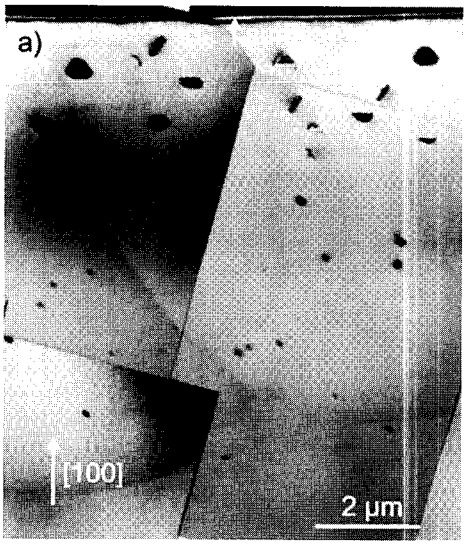
$$D_S^{eq} = \frac{D_{i_S} c_{i_S}^{eq}}{c_S^{eq}}. \tag{2}$$

Under this condition we can determine a constant sulfur diffusion coefficient from errorfunction profiles.

On the other hand, if $D_{i_S} c_{i_S}^{eq} > D_{I_{As}} c_{I_{As}}^{eq}$, then the effective diffusion coefficient is determined by the transport capacity of I_{As},

$$D_S^{noneq} = \frac{D_{I_{As}} c_{I_{As}}^{eq}}{c_S^{eq}} \left(\frac{c_S^{eq}}{c_S} \right)^2. \tag{3}$$

The effective diffusion coefficient depends on the S concentration and gives information about I_{As} diffusion instead of S diffusion. Eq. 3 is an approximation for the case when $c_{i_S} = c_{i_S}^{eq}$ in the whole crystal. For S in-diffusion this is not valid even for long diffusion times. Therefore, the simulations in Fig. 1 were carried out with a set of partial differential equations which describe the diffusion process in the same way as Uematsu et al. [10]. In this non-equilibrium case of S in-diffusion, a supersaturation of I_{As} is produced. TEM investigations of samples annealed at 1100 °C show that small extrinsic dislocation loops were formed during in-diffusion. The density is however so small that they do not considerably influence the diffusion process. At 950 °C the



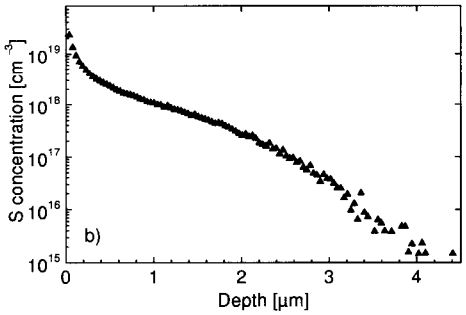


Fig. 2. Sample annealed with 5 μg/cm^3 sulfur in the gas phase at 950 °C for 20 min.
a) TEM cross-section image showing extrinsic stacking faults on {111} planes. The defects reach up to a depth of 9 μm.
b) Sulfur profile measured by SIMS.

behavior is different. Fig. 2a shows a TEM image of a sample annealed at 950 °C with 5 μg/cm^3 sulfur in the gas phase. Large extrinsic stacking faults are found near the surface. A remarkable fact is that the formation of extended defects occurs up to a depth of 9 μm, which is much deeper than the S in-diffusion profile (Fig. 2b). This indicates that the diffusion coefficient of

I_{As} has to be much higher than the diffusion coefficient of i_S. The formation of the extrinsic dislocation loops Φ may be described by one of the following reactions,

$$I_{As} + I_{Ga} \longleftrightarrow \Phi \text{ or } I_{As} \longleftrightarrow \Phi + V_{Ga}. \tag{4}$$

It means that via loop formation the supersaturation of I_{As} is reduced. The second type of reaction results in the formation of Ga vacancies, what may be checked e.g. by positron annihilation. In further investigations we have to determine quantitatively the depth profile of I_{As} condensed in extended defects and to consider in the simulations.

4 In-diffusion of sulfur into dislocation-rich GaAs

An example of the interaction of sulfur with freshly introduced dislocations is shown in the CL micrographs in Fig. 3. Different luminescence channels and contrast types are to be seen. In Fig. 3a dislocations are recognized as dark contrasts. The same dislocations show a bright contrast in Fig. 3b, taken with a Ge detector which has a cut-off wavelength about 850 nm.

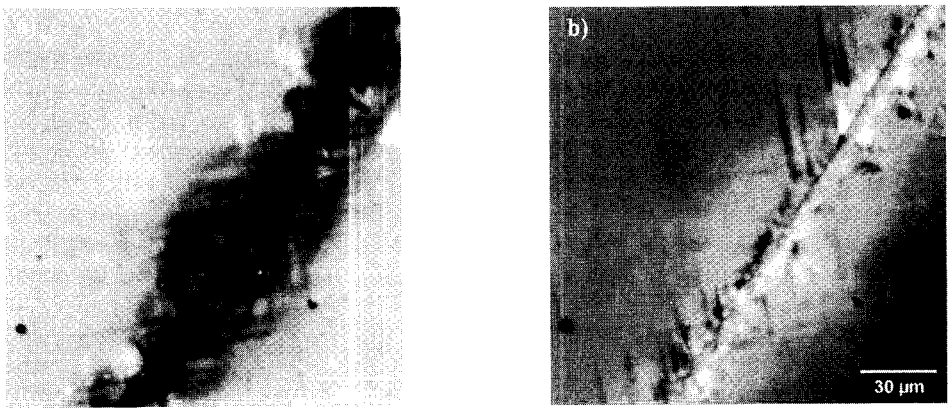


Fig. 3. CL images of SI GaAs after sulfur in-diffusion at 950 °C for 1 h.
a) Image taken with a photomultiplier tube; the band-to-band luminescence at 830 nm is dominating.
b) Image taken with a Ge detector with a cut-off wavelength of about 850 nm.
Dislocations having a dark contrast in a) appear bright in b). The dark features in b) are due to evaporation structures as checked by secondary-electron images.

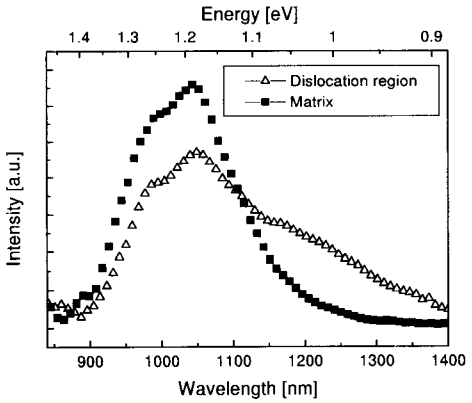


Fig. 4. CL spectra of a GaAs sample after sulfur diffusion at 950 °C for 1 h. The triangles represent the measurement in the undamaged region, the squares belong to the luminescence in the dislocation-rich area.

Fig. 4 shows the spectrally resolved luminescence taken in the damaged region and outside. In the damaged region we found an additional shoulder at about 1200 nm. The luminescence in Fig. 3a can be correlated with the band-band recombination at a wavelength of 830 nm. Dislocations are centers of non-radiative recombination and appear in Fig. 3a with dark contrast. In Fig. 3b we find a luminescence at about 1050 nm which is attributed to a donor-vacancy complex [16]. This complex was formed during the annealing process and is probably identical to $S_{As}V_{Ga}$. It is one possible compensation center which reduces the amount of electrically active sulfur donors. The vacancies for these complexes are provided by reaction Eq. 4. The bright dislocation-related contrasts around the scratch are due to an unidentified defect complex which is enriched near dislocations and which is related to the shoulder in the spectra around 1200 nm. The radiative recombination of this band exceeds the non-radiative channel and dislocations appear bright in Fig. 3b.

Fig. 5 shows the bright-field image and Fig. 6 the intensity ratios of an EDX line scan across a dislocation. The line scan shows an enrichment of sulfur and a decrease in the arsenic concentration around the dislocation.

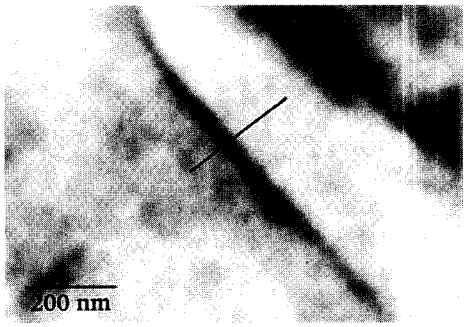


Fig. 5. AEM bright-field image of a dislocation in a sample after sulfur diffusion at 950 °C for 1 h and slow cooling. Across the dislocation we measured the X-ray intensity profiles (line) of Ga, As, and S.

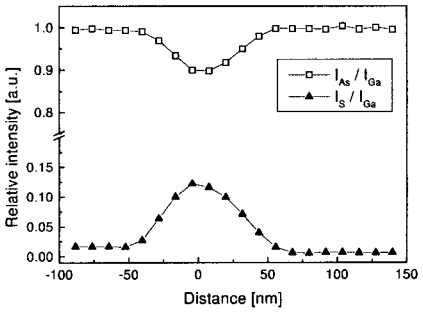


Fig. 6. EDX line scan across the dislocation in Fig. 5. The triangles represent the relative intensities of I_S/I_{Ga}, the squares I_{As}/I_{Ga}. The $L\alpha$ line of Ga and the $K\alpha$ lines of S and As were measured.

After 850 °C for 4 h annealing, only a very weak luminescence was observed. The CL intensity increases with higher annealing temperatures up to a strong luminescence at 1050 °C. These findings can be combined with the TEM results. The extrinsic dislocation loops, which are centers of non-radiative recombination, were found by TEM to be larger and more numerous at lower annealing temperatures.

5 Conclusions

We can describe the sulfur diffusion profiles measured after annealing at 1100 °C by simulations in the same way as Uematsu [10, 15], because of the low density of extended defects. However, at 950 °C we find extrinsic dislocation loops up to a depth of 9 μm. We can conclude for this case, that $D_{i_S} < D_{I_{As}}$. Generally, we found that a complex consisting of a S donor and V_{Ga} was formed. A similar defect complex is also known for Te or Si dopants. The $S_{As}V_{Ga}$ defect is a possible compensation center for the in-diffused sulfur donors. In dislocation-rich GaAs, an additional defect center was formed at dislocations. With AEM we found an enrichment of sulfur near dislocations.

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References

[1] U. Gösele, T.Y. Tan, M. Schultz, U. Egger, P. Werner, R. Scholz, and O. Breitenstein, *Defect Diff. Forum* **143-147** (1997) 1079.

[2] U. Egger, M. Schultz, P. Werner, O. Breitenstein, T.Y. Tan, and U. Gösele, *J. Appl. Phys.* **81** (1997) 6.

[3] M. Schultz, U. Egger, R. Scholz, O. Breitenstein, T.Y. Tan, and U. Gösele, *J. Appl. Phys.* **83** (1998) 5295.

[4] R.F. Scholz, U. Gösele, O. Breitenstein, U. Egger, and T.Y. Tan, *Sol. State Phenom.* **63-64** (1998) 183.

[5] G. Bösker, N.A. Stolwijk, H. Mehrer, U. Södervall, J.V. Thordson, T.G. Anderson, and A. Burchard, *MRS Proc.* **527** (1998) 347.

[6] H. Nishi, *Appl. Phys. A* **67** (1998) 579.

[7] J.-L. Lee, *J. Appl. Phys.* **85** (1999) 807.

[8] M. Noack, K.W. Kehr, and H. Wenzl, *J. Cryst. Growth* **178** (1996) 438.

[9] K. Sonnenberg and A. Altmann, *Mater. Sci. Eng. A* **28** (1994) 481.

[10] M. Uematsu, P. Werner, M. Schultz, T.Y. Tan, and U. Gösele, *Appl. Phys. Lett.* **67** (1995) 2863.

[11] H.S. Leipner, R.F. Scholz, F. Syrowatka, J. Schreiber, and P. Werner, *Phil. Mag. A* in press (1999).

[12] B. Goldstein, *Phys. Rev.* **121** (1961) 1305.

[13] L.J. Vieland, *J. Phys. Chem. Sol.* **21** (1961) 112.

[14] F.C. Prince, M. Oren, and M. Lam, *Appl. Phys. Lett.* **48** (1986) 546.

[15] B. Tuck and R.G. Powell, *Appl. Phys.* **14** (1981) 1317.

[16] E.W. Williams, *Phys. Rev.* **168** (1968) 922.