



Diffusivity of arsenic interstitials in GaAs studied by sulfur in-diffusion

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Abstract

Sulfur in-diffusion, which is governed by the kick-out mechanism, is a suitable tool to study the diffusion on the arsenic sublattice of GaAs. Sulfur diffuses for higher surface concentrations under non-equilibrium conditions of arsenic self-interstitials (I_{As}). The formation of extrinsic dislocation loops has been observed. The loop formation increases the concentration of Ga vacancies, which form complexes with S donors. The presence of such complexes has been investigated by cathodoluminescence, positron annihilation, and electrochemical capacity–voltage profiling. Taking into account the concentration of As interstitials agglomerated in faulted loops, the analysis of the sulfur profile can provide both the diffusion constant and the equilibrium concentration of I_{As} . © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Diffusion on the Ga sublattice of gallium arsenide is important for dopants such as Si, Be, or Zn. Many investigations have been done in this research field, and the diffusion process is quite well understood [1]. However, much less is known for the diffusion of impurities on the As sublattice. Furthermore, the fabrication of electrically homogeneous wafers requires the control of arsenic diffusion and precipitation during post-growth heat treatment. Recently, sulfur as n-type dopant has found increasing interest for device applications [2]. Uematsu et al. [3] concluded that different sets of experimental data of sulfur diffusion can be uniquely described by the kick-out mechanism,

$$i_S \rightleftharpoons S_{As} + I_{As}. \quad (1)$$

i_S stands for sulfur atoms on interstitial lattice sites, S_{As} for sulfur on arsenic sites, and I_{As} for arsenic self-interstitials. Via reaction (1), sulfur diffusion should allow

us in principle to determine the diffusion parameters of As self-interstitials. This requires the careful investigation of the defect reactions caused by in-diffusing sulfur.

2. Experimental details

Semi-insulating liquid-encapsulated Czochralski-grown GaAs was used for sulfur in-diffusion experiments. Annealing was carried out in sealed quartz ampoules after evacuating them to a pressure lower than 10^{-8} bar. To determine the small amounts of sulfur accurately, S was dissolved in benzene. For the results presented here, the sulfur density in the gas phase was $5 \mu\text{g}/\text{cm}^3$. An arsenic pressure of 1 bar during the annealing experiment was established by adding the necessary amount of metallic arsenic to the ampoule. The in-diffusion was performed with various times and temperatures. The samples were either quenched in water or cooled down with a cooling rate of about 6 K/min. S in-diffusion profiles were measured by secondary ion mass spectroscopy (SIMS). The depth distribution of electrically active S, incorporated on As sites as donors, was monitored by electrochemical capacitance–voltage (ECV) profiling. Cathodoluminescence (CL) spectroscopy

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and microscopy were performed with an Oxford Mono-CL system attached to a Tesla BS 300 scanning electron microscope. A liquid-nitrogen-cooled germanium diode, which is sensitive from 800 to 1600 nm, was used as detector. The spectra shown are corrected with the sensitivity curve of the Ge diode. Transmission electron microscopy (TEM) was carried out with a JEOL JEM 1000 high-voltage transmission electron microscope. Additionally, we used a Vacuum Generators HB501-UX analytical electron microscope, equipped with a Kevex energy dispersive X-ray detector. Variable-energy positron annihilation measurements were carried out with a slow-positron beam system using a 0.5 GBq ^{22}Na β^+ emitter assembled with a 5 μm single-crystalline tungsten moderator in transmission geometry [4]. The Doppler broadening of the 511 keV annihilation line was measured as a function of the incident positron energy in the range 0.1–40 keV.

3. Results and discussion

The in-diffusion profiles strongly depend on the boundary conditions, i.e. on the equilibrium concentrations of i_s (c_{is}^{eq}) and S_{As} (c_s^{eq}) at the surface. The equilibrium surface concentration can be adjusted by the sulfur content in the gas phase over the GaAs sample. If the transport capacity of i_s is smaller than or equal to the transport capacity of I_{As} , i.e. $D_{is} c_{is}^{\text{eq}} \leq D_{I_{\text{As}}} c_{I_{\text{As}}}^{\text{eq}}$, then the diffusion proceeds under the equilibrium of intrinsic point defects (arsenic interstitials). In this case, I_{As} are quick enough that always $c_{I_{\text{As}}} = c_{I_{\text{As}}}^{\text{eq}}$. The effective diffusion coefficient is determined by

$$D_s^{\text{eq}} = \frac{D_{is} c_{is}^{\text{eq}}}{c_s^{\text{eq}}}.$$

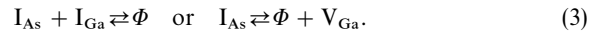
Under this condition, error-function-like profiles and a constant sulfur diffusion coefficient is obtained.

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

$$D_s^{\text{noneq}} = \frac{D_{I_{\text{As}}} c_{I_{\text{As}}}^{\text{eq}}}{c_s^{\text{eq}}} \left(\frac{c_s^{\text{eq}}}{c_s} \right)^2. \quad (2)$$

Eq. (2) is an approximation for the case when $c_{is} = c_{is}^{\text{eq}}$ in the diffused region. For S in-diffusion this is not valid even for long diffusion times, and the whole set of partial differential equations describing the diffusion [3] has to be used to evaluate experimental in-diffusion profiles. Under non-equilibrium conditions of Eq. (2), the diffusion profiles are non-error-function-like. The effective diffusion coefficient depends on the S concentration and provides information about I_{As} diffusion instead of S diffusion. The supersaturation of I_{As} may give rise to the formation of extended defects. TEM investigations of

samples annealed at 1100°C show that small dislocation loops up to 2.5 nm in diameter were formed during in-diffusion. Their density is, however, very small, and they do not considerably influence the diffusion process. The behavior is different at 950°C annealing. Fig. 1a shows a TEM image of a sample annealed at 950°C with 5 $\mu\text{g}/\text{cm}^3$ S in the gas phase. Large loops were found near the surface. The defects were identified with the inside/outside contrast method as extrinsic dislocation loops. They lie on $\{111\}$ lattice planes and are of the Frank type with the Burgers vector $\mathbf{b} = \frac{1}{3}\langle 111 \rangle$. The fringe contrast of the corresponding extrinsic stacking faults is visible in Fig. 1a. The formation of the extrinsic dislocation loops may be described by one of the following reactions:



Via loop formation – Φ stands for a pair of Ga and As atoms in the interstitial loop – the supersaturation of I_{As} is reduced. A remarkable fact is that the formation of extended defects occurs up to a depth of about 10 μm ,

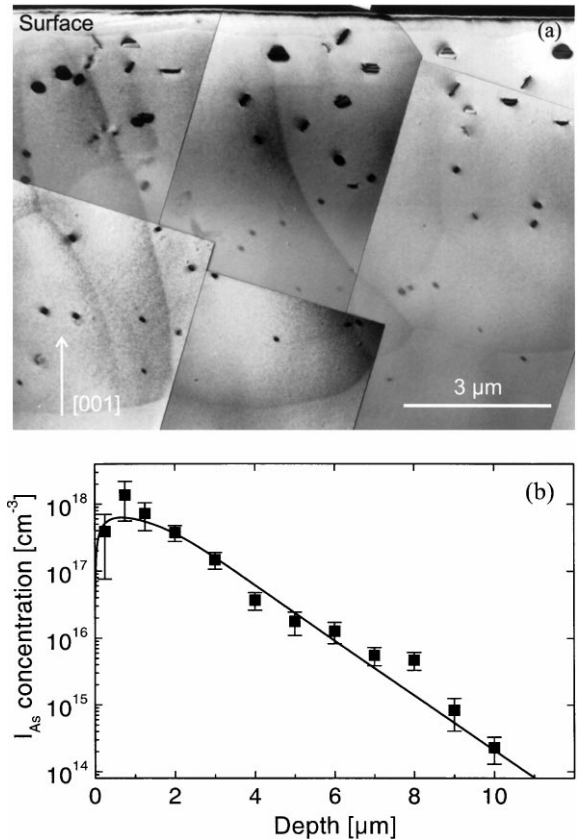


Fig. 1. GaAs sample annealed at 950°C for 20 min. (a) TEM cross-sectional image showing extrinsic stacking faults. (b) Depth profile of As interstitials agglomerated in faulted loops.

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 density of loops has been precisely determined from TEM images covering a large sample area. The size and their depth distribution have been measured. The depth profile of the concentration of I_{As} contained in faulted loops is plotted in Fig. 1b. The error bars mainly result from uncertainties in determining the thickness of the sample foil by counting the number of thickness extinction fringes.

The second type of reaction in Eq. (3) seems to be more likely than the first one, since sulfur in-diffusion leads only to a supersaturation of I_{As} and not of I_{Ga} . Thus, the formation and further growth of faulted loops make the supersaturation of As interstitials decrease at the expense of the formation of Ga vacancies. These vacancies, which are negatively charged acceptors, can form complexes with S donors according to the reaction



Similar defect complexes have been discussed for impurities such as Te, Sn, and Se. They exhibit a deep center luminescence band in the region 1.2–1.3 eV. It is thought to be a localized transition in the donor- V_{Ga} complex, the ground state of which is derived from the vacancy and the excited state in the configuration coordinate model from the donor [5].

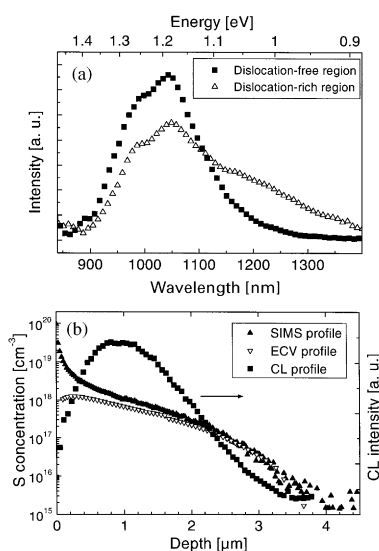


Fig. 2. Cathodoluminescence of GaAs samples after sulfur diffusion at 950°C. (a) CL spectra taken at 77 K in a dislocation-free and dislocation-rich region. (b) Depth profile of the peak intensity of the 1.2 eV CL band compared to the SIMS and the ECV profiles (diffusion time 1 h).

In dislocation-rich areas, an additional shoulder around 1 eV appears in the luminescence spectra (Fig. 2a). This may be related to the accumulation of sulfur and the depletion of arsenic at dislocations, which was found by analytical electron microscopy [6]. Various sulfur-rich phases or centers are under consideration for the 1 eV shoulder.

Fig. 2b compares the depth distribution of the in-diffused total amount of sulfur, as measured by SIMS, with the profile of the electrically active S_{As} , which has been determined by ECV profiling. The maximum S donor concentration amounts to $1.5 \times 10^{18} \text{ cm}^{-3}$. The discrepancy between the total S concentration and the concentration of S_{As} may be explained by various compensation mechanisms. Two processes may be discussed here: the formation of sulfur clusters or precipitates and the formation of compensating $S_{As}V_{Ga}$ complexes. The former process has been observed preferably at dislocations introduced by plastic deformation [6]. It may play a minor role in as-grown GaAs wafers with a dislocation density of about 10^4 cm^{-2} . Thus, the main mechanism of electrical inactivation of in-diffusing sulfur is the formation of donor vacancy complexes via reaction (4). The depth profile of the intensity of the 1.2 eV CL line, which has been measured at a cross-sectional sample, is shown in Fig. 2b. At a depth of 2.5 μm the relative intensity decreases to 1/e, indicating that the concentration of $S_{As}V_{Ga}$ complexes becomes low. This corresponds to the course of the SIMS and ECV profiles, which indicate that for a depth $> 2.5 \mu\text{m}$ the total S concentration equals roughly the concentration of electrically active sulfur. It should be noted that the drop in the CL intensity near the sample surface (depth below 500 nm) is related to a so-called dead layer of non-radiative recombination, which is caused by the pinning of the Fermi level by surface states and a space-charge region.

The question, whether gallium vacancies are released as a result of the in-diffusion of sulfur and the formation of faulted loops has been investigated by positron annihilation measurements. The S and W line shape parameters, which describe the Doppler broadening of the 511 keV annihilation line, have been measured as a function of the incident positron energy. The W parameter is distinctly lower in GaAs after sulfur in-diffusion. Accordingly, the S parameter increased. It is well known that this behavior can be described by the presence of vacancy-type defects [7]. Dependent on the annealing conditions (temperature and time), vacancies have been observed within a depth of 1–3 μm from the surface. As a result of the loop formation (3), vacancies may be also expected in a depth of up to 10 μm . However, it can be concluded from the positron results that in this region, V_{Ga} are not thermally stable. Such stable defects only appear in a region where the reaction (4) or the formation of other vacancy-sulfur complexes is possible.

In conclusion, the in-diffusion of sulfur results in the supersaturation of As interstitials, which may lead to the formation of interstitial dislocation loops. On the other hand, the supersaturation of I_{As} is reduced at the expense of the production of Ga interstitials. The latter gives rise to the compensation of S donors via the formation of $S_{As}V_{Ga}$ complexes. The influence of the formation of faulted loops on the shape of the diffusion profiles and hence on the diffusion parameters has been investigated [8]. It has been found that the tail of the profile depends on both factors contained in the transport capacity, i.e. on the diffusivity and the concentration of I_{As} . As a result of the simulation [8], the diffusivity of I_{As} has been determined. It amounts to $6.8 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for 950°C , while $c_{I_{As}}^{\text{eq}} = 3 \times 10^{14} \text{ cm}^{-3}$. The effective diffusion

constant of i_s has been found to be $2.8 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for that temperature.

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