Interaction of Copper with Dislocations in GaAs

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Abstract. — The interaction of copper with dislocations was studied in silicon-doped gallium arsenide by means of cathodoluminescence, analytical, and transmission electron microscopy. Several structures of defect complexes or microdefects surrounding the dislocations were found depending on the diffusion temperature and cooling rate. The results could be explained by considering the local nonequilibrium of intrinsic point defects induced by Cu in- or outdiffusion. The appearance of a bright or dark dislocation contrast in the cathodoluminescence pictures is related for different diffusion conditions: i) to the enrichment of copper acceptors at dislocations, ii) to the distribution of silicon-vacancy complexes, and iii) to non-radiative recombination at Cu-As precipitates or clouds of small dislocation loops.

Introduction

The behavior of copper in semiconductors is of importance, since it may be introduced as an unwanted metallic impurity during crystal growth or subsequent processing steps [1]. In gallium arsenide, copper has two levels in the band gap and thus a significant influence on electronic properties. However, the concentration of electrically active Cu is much lower than the total concentration incorporated [2,3]. The reason is the low solubility of Cu in GaAs at room temperature. The electrically inactive copper forms precipitates [3].

Dislocations are known as effective gettering centers of impurities [4,5]. The subject of the study presented here is the interaction of copper with dislocations in GaAs. Investigations of the luminescence properties of copper-decorated dislocations are supplemented by analytical and Transmission Electron Microscopy (TEM).

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Table I. — Annealing conditions of copper-diffused GaAs:Si samples (T annealing temperature, t annealing time, v cooling rate).

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**Experimental Details**

A layer of fresh dislocations was prepared by scratching the (001) surface of Bridgman-grown silicon-doped GaAs wafers (carrier concentration about 2 × 10¹⁷ cm⁻³). The density of dislocations introduced by the local damage was low enough that in most cases individual dislocation lines could be recognized by cathodoluminescence (CL) imaging. The motion of the dislocations from their sources near the scratches up to a distance of about 150 µm was thermally activated by a short heat treatment at 623 K for 600 s. After evaporating a 50 nm copper layer on the surface, the samples were annealed at different temperatures T in closed ampoules with equilibrium arsenic pressure. The annealing time t was chosen in such a way that a homogeneous Cu concentration was established in the whole sample, according to the diffusion coefficient D of Cu in GaAs of 0.03 cm²s⁻¹ exp \(-\frac{0.53 \text{ eV}}{k_B T}\) given by Hall and Racette [6] (k_B Boltzmann constant). The samples were cooled down to room temperature either by quenching in water or by furnace cooling. The annealing conditions are summarized in Table I. After the pre-treatment, the samples were chemically polished for further examination. CL spectroscopy and imaging were carried out in a Tesla BS300 scanning electron microscope equipped with a liquid-helium cooling stage and an Oxford Mono-CL system. The spectra were recorded with a liquid-nitrogen-cooled Ge detector and corrected with the corresponding sensitivity curve of the detector.

In order to investigate the composition of agglomerates near dislocations, energy-dispersive X-ray (EDX) analysis was carried out in a VG HB501UX scanning transmission electron microscope (STEM) operating at 100 kV. Additionally, the structure of defects was investigated in TEM bright-field diffraction contrast in an 1000 kV Jeol transmission electron microscope.

**Results**

CL spectra of the samples LF and HF (see Tab. I) are shown in Figure 1a. The LF sample exhibits in addition to the exciton luminescence line of GaAs at 1.51 eV [7], which is the only one found in untreated GaAs:Si, the Cu-acceptor peak (Cu²⁺) at 1.36 eV. The panchromatic CL distribution of the LF sample is similar to an as-grown sample without Cu diffusion, i.e. dark dislocation contrasts are found. No bright halos around dislocations were identified. The similarity of the CL picture of the LF sample to the untreated one can be related to the fact that the 1.51 eV peak is dominating the image (Fig. 1a). Undecorated glide dislocations were found by TEM. In the matrix a random distribution of dislocation loops with a density of about 1 × 10¹³ cm⁻³ was visible. These microdefects were identified by the inside/outside contrast procedure [8] as dislocation loops of interstitial type.

Only the 1.36 eV peak appeared after Cu diffusion at 1373 K and quenching (sample HF). Figure 1b shows for this case a panchromatic CL picture of dislocations near a scratch. Bright
dislocations are surrounded by dark halos, indicating high Cu concentrations at the dislocation lines surrounded by Cu-depleted regions. The CL intensity of the HF sample is supposed to be a direct measure of the concentration of Cu, since the 1.36 eV peak associated with $\text{Cu}_{\text{Ga}}^{2-}$ acceptors dominates the spectra. On the dislocations a high number of small precipitates were identified. They are easily recognized in the STEM (Fig. 1c), but hardly visible in TEM diffraction contrast. The diameters of the precipitates are 20 to 30 nm, and their average distance amounts 200 nm. A few precipitates with diameters of 15 to 20 nm were found in the matrix.

The $\text{M}_1\text{F}$ sample shows a defect configuration similar to the LF sample. In the $\text{M}_2\text{F}$ sample a small number of precipitates occurred only on dislocations.

The behavior of the slowly cooled samples is more complex than the quenched ones. In the LS sample the spectra are dominated by the luminescence band at 1.27 eV (Fig. 2a), which has been related to a silicon-vacancy complex [7], $(\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}})^-$. The panchromatic CL picture

Fig. 1. — Spectra and pictures of copper-diffused GaAs samples after quenching. a) Cathodoluminescence spectra measured at 70 K of the samples LF (thick line) and HF (thin line), respectively. b) Panchromatic cathodoluminescence picture (20 kV, 1 nA) of sample HF at 10 K (D - dislocations). c) STEM picture of sample HF.
Fig. 2 — Spectra and pictures of the sample LS. a) Cathodoluminescence spectrum measured at 70 K. b) Panchromatic cathodoluminescence pictures (20 kV, 1 nA) at 300 K. c) TEM bright field image (D indicates dislocations and C the colonies of small dislocation loops in the bulk)

shows dark dislocation contrasts with bright surroundings (Fig. 2b). There are also many dark spots in the matrix area. A typical TEM defect picture of the sample LS is shown in Figure 2c. A cylinder of microdefects around dislocations is visible. These microdefects were identified by the inside/outside contrast rule as dislocation loops of mainly interstitial type. A few loops of vacancy type appear as well. In the matrix the loops form colonies. It was proved by a 1:1 correlation of the same sample area that the dark spots in the CL pictures are the colonies of small dislocation loops in the TEM images.

The spectra of the HS sample does not differ significantly from that in Figure 2a and they are hence also dominated by the luminescence band at 1.27 eV. The panchromatic CL picture shows extended dark halos surrounding the dislocations (Fig 3a). The dislocations themselves are bright. No characteristic contrast appears in the matrix region. In the TEM bright-field image (Fig. 3b) many precipitates with a diameter of up to 200 nm on the dislocations or in close vicinity are visible. It is concluded that precipitates are formed preferentially on dislocations.
Fig. 3. — a) Panchromatic cathodoluminescence picture of sample HS measured at 20 kV, 1 nA, and 300 K (D - dislocations, S - scratch). b) TEM bright-field image of dislocations with precipitates near the scratch.

Fig. 4. — Composition measured for a particle in sample HF. The symbols are the measured values for Ga, As, and Cu. The lines represent the fits for the determination of the actual composition of the precipitate.

As a result of climb processes dislocations frequently move away from the precipitates.

In order to determine the composition of the precipitates on dislocations, EDX analysis was carried out with a spatial resolution in the nm range. The concentrations of As, Ga, and Cu measured at one precipitate in sample HF are given in Figure 4. However, the composition obtained from the EDX measurement does not reflect the true composition in the precipitate. In order to separate the contributions of the matrix and the particle, the concentrations of the three constituents \( i \) were fitted according to

\[
c_i = \frac{V_p}{V} c_i^p + \frac{V - V_p}{V} c_i^m,
\]

\( c_i \) is the concentration of As, Ga, or Cu, respectively. \( V \) the total volume excited by the electron beam and \( V_p \) the volume of the particle assumed as a sphere. \( c_i^p \) and \( c_i^m \) are the concentrations...
of the constituents in the particle and in the matrix, respectively. For the calculation of the interaction volume $V$, a spreading of the beam radius $r$ according to $r(z) \propto z^{3/2}$ was taken into account (z depth). The sample thickness was calculated from the electron energy loss spectra [9].

The composition of the precipitates on dislocations was found for a number of HF and HS samples in the range of 62 ... 75 atom% copper and 38 ... 25 atom% arsenic, respectively. Virtually no Ga was detected within the error limits of about 5 atom%. In the low-temperature phase diagram of Cu-Ga-As only one stable As-rich compound exists in thermodynamic equilibrium, viz. Cu$_3$As [10]. However, the non-equilibrium state on the dislocation may influence the actual composition. One may also conclude that the As-rich copper precipitates on dislocations are an agglomerate of a pure As phase and Cu$_3$As. Further investigations on the crystallographic structure of the particles by electron diffraction and high-resolution TEM are under way.

The composition of particles in the LS sample has been estimated only qualitatively. Here a greater proportion of gallium of up to 35 atom % and a corresponding lower As content was found.

Discussion

The formation of copper precipitates on dislocations in gallium arsenide was studied according to its dependence on the diffusion temperature and cooling rate. The interpretation of the effects requires the consideration of the influence of copper on the equilibrium of intrinsic point defects.

We discuss first the effects in the samples quenched after Cu diffusion.Interstitial copper Cu$_1^+$ is assumed to diffuse via the kick-out mechanism [11, 12],

$$\text{Cu}_1^+ \rightarrow \text{Cu}_{Ga}^2^- + \text{Ga}_1^{2+} + h^+. \quad (1)$$

The luminescence peak related to the Cu$_{Ga}^2-$ acceptor was identified in the CL spectra (Fig. 1a). At the rather low diffusion temperature of the LF sample, a supersaturation of Ga interstitials Ga$_1^{2+}$ occurs during the indiffusion of Cu. These defects are condensing to interstitial loops via the reaction Ga$_1^{2+} + \text{As}_1^- \rightarrow \Phi(\Delta l, \Delta A) + 2h^+.$

$\Delta\Phi(\Delta l, \Delta A)$ means that a dislocation loop changes its length by $\Delta l$ and/or the area by $\Delta A$. Additionally, arsenic interstitials As$_1$ are required for the loop formation. However, the concentration of As$_1$ is expected to be rather low in the investigated Bridgman GaAs [13], so that the loop formation leads to the emission of arsenic vacancies:

$$\text{Ga}_1^{2+} \rightarrow \Phi(\Delta l, \Delta A) + V_{As}^+ + h^+. \quad (2)$$

The loops can be observed in the TEM images after quenching the sample to room temperature. However, the quenching time of the LF sample is too short for formation of Cu precipitates. Furthermore, the solubility changes only by one order of magnitude [6] during the cooling from 943 K ($1 \times 10^{17}$ cm$^{-3}$) to 300 K ($1 \times 10^{16}$ cm$^{-3}$).

The equilibrium conditions are different at the high diffusion temperature of sample HF. The solubility of Cu at 1343 K is over three orders of magnitude higher ($7 \times 10^{19}$ cm$^{-3}$) compared to the solubility at room temperature. This is the reason why the conductivity changes to p-type, whereas after diffusion at 973 K, the sample is still n-type.

The equilibrium concentration of charged point defects depends on the doping level (Fermi-level effect). In the quasi-chemical reactions of this paper the most probable charge states of the point defects under given conditions are indicated. In the model of Tan and Gösele [11, 12], the
equilibrium concentration of the doubly positively charged Ga interstitials, \( c_{Ga_i^{2+}}^{eq} \), is obtained as a function of the carrier concentration \( p \):

\[
c_{Ga_i^{2+}}^{eq} = c_0 \left( \frac{p}{n_i} \right)^2.
\]

(3)

\( c_0 \) is the concentration of interstitials for the intrinsic carrier concentration \( n_i \), \( c_0 = c_{Ga_i^{2+}}^{eq}(n_i) \).

Furthermore, the number of Ga interstitials is a function of the temperature and the vapor pressure \( P_{As_4} \) (assumed to be dominated by \( As_4 \)), \( c_{Ga_i^{2+}}^{eq} = c_{Ga_i^{2+}}^{eq}(p, T, P_{As_4}) \).

A higher equilibrium concentration of \( Ga_i^{2+} \) is established according to equation (3) after diffusion of Cu in sample HF, since \( p \) increases. Thus, no condensation of excess interstitials to loops could be observed. If the sample is quenched from 1343 K, copper must form precipitates because of the jump in solubility. The quenching process takes several seconds, which is enough for Cu to move some micrometers. In this time Cu can go to the dislocations and form there small precipitates. The enrichment of copper in the elastic strain field of dislocations is visible in the CL pictures (Fig. 1b). No equilibrium state can be achieved, because the precipitates as impurity sinks grow further. This is the reason for the extended zone depleted of Cu (dark zone surrounding the dislocations in Fig. 1b), which has a range over some micrometers. It should be mentioned that a normal Cottrell atmosphere has only an extension of some nanometers. In case the copper cannot reach a sink, then precipitates are formed in the bulk, too.

If the sample is cooled down slowly (samples LS and HS) then the concentration of Cu is expected to decrease by outdiffusion. This means that Cu diffuses to possible sinks (dislocations, loops, or surfaces). During this process, Ga vacancies are left behind in the matrix, \( Cu^{2-}_Ga + e^- \rightarrow V^{3-}_Ga + Cu_{sink} \). The Ga vacancies may react with \( Si^{+}_{Ga} \) donors to form complexes [14,15]:

\[
Si^{+}_{Ga} + V^{3-}_Ga \rightarrow (Si_{Ga}V_{Ga})^- + e^-.
\]

(4)

This complex having the CL band at 1.27 eV dominates the CL spectra and images in the samples LS and HS (Figs. 2a, b).

The diffusion of copper to the dislocations during the slow cooling of sample LS is related via the kick-out mechanism of reaction (1) to a supersaturation of Ga interstitials around dislocations. A cylinder of interstitial loops surrounding the dislocations is formed, which is again a sink for copper. Additionally, the Ga-rich surrounding of the dislocation may be responsible for the higher Ga content found in the precipitates of sample HS. The As vacancies emitted by the loop formation (2) may react with \( Ga_i \) to form \( Ga_{As} \) antisites.

A similar mechanism of interstitial supersaturation occurs around existing small loops in the matrix. New interstitial loops are formed and finally colonies of dislocation loops can be observed (Fig. 2c).

In sample HS, the outdiffusion of Cu during the slow cooling occurs similar to sample LS. No supersaturation of Ga interstitials occurs and thus no loops are formed as in sample HF, since \( c_{Ga_i^{2+}}^{eq} \) is higher according to equation (3). The longer cooling time results in the formation of larger precipitates on dislocations. This can be illustrated by the diffusion coefficient related to the cooling rate, \( D(T)/v \). This ratio amounts \( 4 \times 10^{-4} \text{ cm}^2 \text{ K}^{-1} \) for the LS sample and \( 8 \times 10^{-4} \text{ cm}^2 \text{ K}^{-1} \) for the HS sample. The ratio is distinctly smaller for the samples HF and LF (\( 1 \times 10^{-6} \text{ cm}^2 \text{ K}^{-1} \) and \( 1 \times 10^{-7} \text{ cm}^2 \text{ K}^{-1} \), respectively) with small or virtually no precipitates. One should keep in mind however that the diffusion coefficient near the dislocations may be
drastically changed. With the composition for the precipitates obtained from EDX analysis, the following reaction is expected:

\[ 3\text{Cu}^+ + 2\text{Ga}_\text{Ga} + 2\text{As}_\text{As} \rightarrow (\text{Cu}_3\text{As})_p + 2\text{Ga}_2^2+ + \text{As}_1 + h^+. \] (5)

In this reaction the equilibrium composition of \((\text{Cu}_3\text{As})_p\) has been assumed for the particle. Two Ga atoms are included on the left side of the reaction for stoichiometrical reasons. The further growth of the precipitate requires the emission of Ga and As interstitials, which has already been included in reaction (5). Dislocation climb, which is due to these interstitials near the dislocation, becomes visible in the TEM images of sample HS (Fig. 3b). Part of the Ga\(_I\) can diffuse away from the dislocation during the cooling and react with the vacancies formed by the outdiffusion of copper to the sinks. Thus in the CL image, which is dominated by the donor-vacancy complex, a dark cloud surrounding the dislocation can be seen (Fig. 3a), because there are less vacancies to form the complexes of reaction (4).

**Conclusions**

In the temperature range under investigation, the diffusion coefficient of Cu in GaAs is slightly higher than in silicon, as given by Hall and Racette [6]. In difference to silicon [16,17], the formation of copper colonies in the matrix and associated dislocation tangles could not be observed in GaAs.

The observed effects can only be explained consistently by assuming the fast kick-out mechanism for the diffusion of copper in GaAs. The high density of self interstitials condensed in loops cannot be related to a pure interstitial mechanism or to the diffusion via vacancies.

The complex behavior of copper at dislocations can be only treated in GaAs by taking into account the local change of the equilibrium conditions of intrinsic point defects by copper diffusion. Dislocations are sinks for Cu\(_{\text{Ga}}^2+\) acceptors, what may become visible in cathodoluminescence images of quenched samples. Furthermore, they are preferred nucleation sites for the formation of precipitates. Dislocations are able to change the point-defect concentration in a region extended over several micrometers. The reason for this is the very fast Cu diffusion.

The kick-out mechanism of copper diffusion is responsible for a supersaturation of Ga interstitials. Three distinct effects are to be observed in dependence on the diffusion conditions:

- formation of dislocation loops,
- dislocation climb,
- change in the composition of the precipitates.

In slowly cooled samples, the formation of the \((\text{Si}_{\text{Ga}}\text{V}_{\text{Ga}})\) complex can be observed by CL. In connection with the changed point-defect concentration, the concentration of this center is distinctly different to the matrix concentration in the surrounding of dislocations.

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References