Study of vacancy-type defects after Cu diffusion in GaAs

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Abstract

Semi-insulating GaAs was contaminated by Cu. For this purpose, a thin Cu layer (30nm) was deposited by evaporation. The diffusion and the homogeneous distribution of the Cu was performed during an annealing step at 1100°C under defined As vapour pressures. The samples were quenched to room temperature. During a subsequent isochronal annealing experiment, vacancy clusters were found to be created, grown, and finally disappeared. The number, size, and distance depend on the annealing temperature and quenching speed. Positron lifetime measurements show that the clusters contain more than 10 vacancies. Moreover, Doppler-coincidence spectroscopy shows clearly that the clusters are surrounded by Cu atoms. The association of Cu-rich precipitates and voids with a diameter of up to 50nm could be evidenced by analytical transmission electron microscopy. The smaller clusters have a crystallographic shape, while larger voids are spherical with a Cu-rich shell. The particles are frequently bound to dislocations. A possible model related to the out-diffusion of copper and the agglomeration of the formed vacancies is discussed.

1. Introduction

Copper is one of the most common unintentional impurities in semiconductors. It diffuses rapidly even at low temperatures by interstitial diffusion process (the so-called kick-out mechanism) [1]. The diffusion coefficient in GaAs was reported to be as high as $D = 1.1 \times 10^{-5} \text{cm}^2\text{s}^{-1}$ at 500°C [2]. The solubility was found also to be rather high $-2 \times 10^{16} \text{cm}^{-3}$ at 500°C and $7 \times 10^{18} \text{cm}^{-3}$ at 1100°C [2].

In GaAs copper acts as a double acceptor, being incorporated at a substitutional lattice site as a CuGa. But in spite of high solubility only a small fraction of the total Cu concentration is electrically active as acceptor after cooling to room temperature. The major part forms Cu–Ga precipitates [3].

In an earlier work [4] it was shown that vacancy clusters are formed during the post-annealing of the GaAs contaminated with Cu by diffusion. It was assumed that the copper atoms surround these clusters. The present paper is the continuation of the previous positron annihilation study of the Cu in- and out-diffusion in GaAs. The presence of Cu precipitates–vacancy cluster complexes was confirmed by transmission electron microscopy (TEM) and Doppler coincidence spectroscopy. We will show also that Cu out-diffusion depends on the in-diffusion conditions, in particular on the arsenic pressure during Cu diffusion.

2. Experimental details

Undoped semi-insulating GaAs samples of thickness 0.4mm were covered by 30nm Cu by evaporating it under UHV conditions. This corresponds to a volume concentration of $6 \times 10^{18} \text{cm}^{-3}$ which is approximately the upper solubility limit of Cu in GaAs. The thickness of the deposited layer was controlled by a thickness

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measurement device (frequency shift of a crystal oscillator). After Cu deposition at one surface, the samples were annealed in a two-zone furnace at 1100°C under different arsenic pressure (0.2–10 bar) for 3h corresponding to a Cu diffusion length of about 1.5 cm. After annealing, the samples were quenched in the quartz ampoules into water at room temperature. The samples were measured in the as-quenched state by Hall effect and thermoprobe measurements. Thereafter, the samples were isochronally annealed in the temperature range up to 900 K. The samples were cooled down slowly after each annealing step. After each annealing step positron annihilation lifetime, Doppler-broadening spectroscopy, and Hall-effect measurements were performed. The resolution of the spectrometers was 240 ps and 1.4 keV, respectively. The GaAs crystals were oriented with their (110) axis towards the Ge detector. The samples were investigated with TEM and energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

Our semi-insulating undoped GaAs sample did not show any positron trapping. After Cu in-diffusion a small increase in the average positron lifetime in the high-temperature region was observed. In Fig. 1 the temperature-dependent measurements of the average positron lifetime after different annealing steps are shown. All the curves demonstrate a strong decrease of the average lifetime at low temperatures. This is a typical dependence for shallow positron traps, which tend to trap positrons in the extended region of the Coulombic potential, reflecting thereby the properties of the bulk [5]. At high temperatures, the existence of shallow traps can be neglected due to the high detrapping rate. In the case of copper in-diffusion these traps must be the Cu acceptors, whose concentration is up to $3 \times 10^{17}$ cm$^{-3}$ according to the Hall-effect measurements (Fig. 2c).

During the first annealing steps, average positron lifetime increases significantly up to the value of 273 ps, indicating the presence of vacancy-type defects. With a further increase of the annealing temperature we observed a rapid decrease of the average positron

![Fig. 1. Average positron lifetime as a function of sample temperature in undoped GaAs. Prior to the experiment, about $6 \times 10^{18}$ cm$^{-3}$ Cu atoms were introduced by evaporating 30 nm Cu to the sample surface and by a subsequent annealing at 1100°C under 2.62 bar of As pressure (3h, quenched into water). The lifetime experiment was performed after each annealing step as indicated in the figure.](image1)

![Fig. 2. Positron lifetime results of the annealing experiments of undoped semi-insulating GaAs sample after in-diffusion of $6 \times 10^{18}$ cm$^{-3}$ Cu atoms at the 2.62 bar As vapour pressure: (a) average positron lifetime. (b) defect-related lifetime. The spectra were measured at 466 K. (c) Hall-effect measurements after each annealing step.](image2)
lifetime. This annealing behaviour of the average and defect-related lifetime is presented in Fig. 2a and b. It can be seen that the open volume of the detected objects increases during annealing. The defect-related lifetime is much higher than that for monovacancy (250–260 ps) [5] and may only be explained by positron trapping at large microvoids. The value of 480 ps corresponds to the clusters, which contain more than 10 vacancies. It was assumed that these clusters are decorated by Cu precipitates [4]. However, this cannot be concluded from positron lifetime results alone.

Fig. 3 shows the high momentum part of the positron annihilation momentum distribution, normalized to the GaAs:Zn reference. The upper part presents the curve for pure Cu, the lower contains three curves: one for Si$_{Ga}$–V$_{Ga}$ complex, corresponding to the Ga monovacancy, and the other two for GaAs contaminated with Cu in as-quenched state and after annealing at 500 K. It is obvious that the shape of GaAs:Cu momentum distribution is very similar to the one for pure Cu. This means that copper atoms surround the observed positron trapping centres.

The presence of such vacancy cluster–Cu precipitate complexes was found also by TEM performed together with the EDX measurements in all the samples after Cu in-diffusion and after further annealing. The results are presented in Fig. 4. One can see large vacancy clusters (light spot on the picture) surrounded by copper atoms and neighboured by a copper precipitate. These clusters were observed for all samples after copper in-diffusion and after each annealing step. However, the distance between them is much higher than the mean positron diffusion length, so they should be invisible for positron annihilation. The large voids were earlier also found in GaAs after Zn in-diffusion [6].
Thus, we have two types of cluster–copper complexes: the relatively small number of large clusters after in-diffusion of copper, and the large number of smaller clusters after the applied annealing procedure, that are formed during out-diffusion of copper atoms. That means that CuGa atoms dissolved during the annealing begin to leave their sites and form precipitates which are connected with vacancy clusters. This out-diffusion process can be seen clearly in Fig. 2c where the minimum of the hole concentration corresponds to the maximum of the defect-related lifetime, i.e. to the maximum size of the vacancy clusters. The origin of these clusters is easy to understand taking into account that the atomic density of GaAs (4.43 × 10^{22} \text{cm}^{-3}) is two times smaller than the atomic density of Cu (8.48 × 10^{22} \text{cm}^{-3}). Therefore, when Cu leaves the Ga sublattice and forms precipitates some open-volume defects must be formed. In the first place these are Ga vacancies. But according to the large defect lifetime, vacancies in both sublattices must be involved. That means that As atoms must go into the interstitial region. If it is so this process should be dependent on the quantity of the excess As in GaAs, i.e. on the stoichiometry. This was indeed observed.

Fig. 5 shows the results of the same annealing experiments for the samples that were contaminated with Cu at different As pressures (0.2–10 bar). The lower the As pressure during in-diffusion is (As deficiency), the easier the arsenic goes into the interstitial region, and the more remarkable is the process of voids formation (the maximum of the average positron lifetime is higher).

After annealing at 850 K the vacancy signal for all of the samples disappears. It is possible that the small vacancy clusters are dissolved at this temperature. But in this case the hole concentration should have a sharp increase at this temperature. That was not observed (Fig. 2c). Another probable reason is that small clusters combine with each other forming large voids with the distance between them being much longer than the mean positron diffusion length and thus become invisible for positron annihilation.

4. Conclusion

Positron annihilation together with electron microscopy and electrical measurements was used to study undoped semi-insulating GaAs after Cu in-diffusion and during Cu out-diffusion. To summarize our experimental finding we can state the following:

- large vacancy clusters surrounded by Cu atoms and neighboured by Cu precipitates are formed during Cu in-diffusion and cooling; almost no positron trapping is found after quenching from diffusion temperature,
- during annealing, vacancy clusters decorated with Cu atoms are formed and grow up to a size more than 10 vacancies with increasing annealing temperature,
- according to the Hall-effect measurements the process of formation of these clusters relates to the Cu out-diffusion,
- as far as the vacancies in both sublattices must be involved the creation of the open-volume defects should be dependent on the stoichiometry of the GaAs system. A smaller quantity of excess As should support the formation of vacancy cluster, i.e. it is more simple for As atoms to go into interstitial region,
- with annealing at temperatures higher than 850 K the vacancy clusters grow and the distance between them becomes larger than the diffusion length of they positron: they become invisible for positron annihilation.

References