Detection of Vacancy-Like Defects during Cu Diffusion in GaAs by Positron Annihilation

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Introduction

The thermodynamic analysis acts as an approach that allows predicting the concentration of the point defects incorporated into crystals under equilibrium conditions. In this work we investigated the point defects quenched from different equilibrium states by means of positron annihilation lifetime spectroscopy. In many cases it is difficult to conclude from the annihilation parameters alone which defect is responsible for the positron trapping. The basic thermodynamic consideration displayed in this paper helps us in characterizing the origin of the observed vacancy-complex. Cu is a rapidly diffusing contaminant already at low temperatures. Cu diffuses very fast by kick-out mechanism and exhibits unusually large diffusion coefficient in many semiconductor crystals.

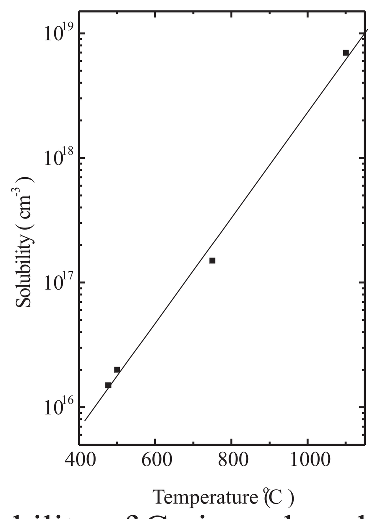

Figure 1. Solubility of Cu in undoped GaAs as a function of temperature (Ref. 1).

Experimental Work

The SI GaAs samples were covered by 30 nm Cu by evaporation. The samples and pure arsenic were sealed in quartz ampoules under high vacuum. Annealing was performed at 1100 °C.

The temperature of the arsenic source was varied in the region of 550 - 740 °C (0.2 - 9.68 bar of As vapor pressure). After annealing the samples were quenched in RT water. The samples were subject to Hall effect measurements. Thereafter, the samples were isochronally annealed in the temperature range up to 850K. The samples were cooled down relatively slow after each annealing step and subject to PAL measurements.The samples annealed at 0.2 and 9.68 bar of P_{As} were chosen for titration analysis.

Result and Discussion

The SI GaAs (reference sample) did not show any positron trapping. After Cu in-diffusion the average lifetime (τ_{av}) increases slightly in the region of high temperature (vacancies generation). The decrease of τ_{av} with decreasing the temperature is a typical dependence for shallow positron traps (ionized Cu acceptor) Fig. 2 [2].

With annealing at temperatures higher than 800 K the vacancy signal disappear and this is may be due to the fact that vacancies clusters grow and the distance between them became larger than the positron diffusion length. Thus, they become invisible for positrons [3].

The open volume of the detected vacancy like-defect increases with increasing the annealing temperature (Fig. 3) but still lies in the monovacancy region until 750 K. τ_d reaches the value of 332 ps at 800 K what corresponds to a vacancy cluster of two vacancies (the upper panel of Fig. 4).

The lower panel of figure 3 represents the defect concentration versus the annealing temperature where the defect concentration is determined according to Eq. (1).

$$K_d \quad \mu C = \frac{1}{\tau_b} \frac{\tau_{av} \quad \tau_b}{\tau_d \quad \tau_{av}} . \qquad (1)$$

The number of vacancies is one in the temperature range up to 750 K and increases to be 2 vacancies at 800 K (Fig. 4). This was concluded according to the calculation following Ref. [4].

One sample was not treated with Cu and annealed under very similar condition (Fig. 5). The as-quenched sample shows the maximum value of τ_{av}.

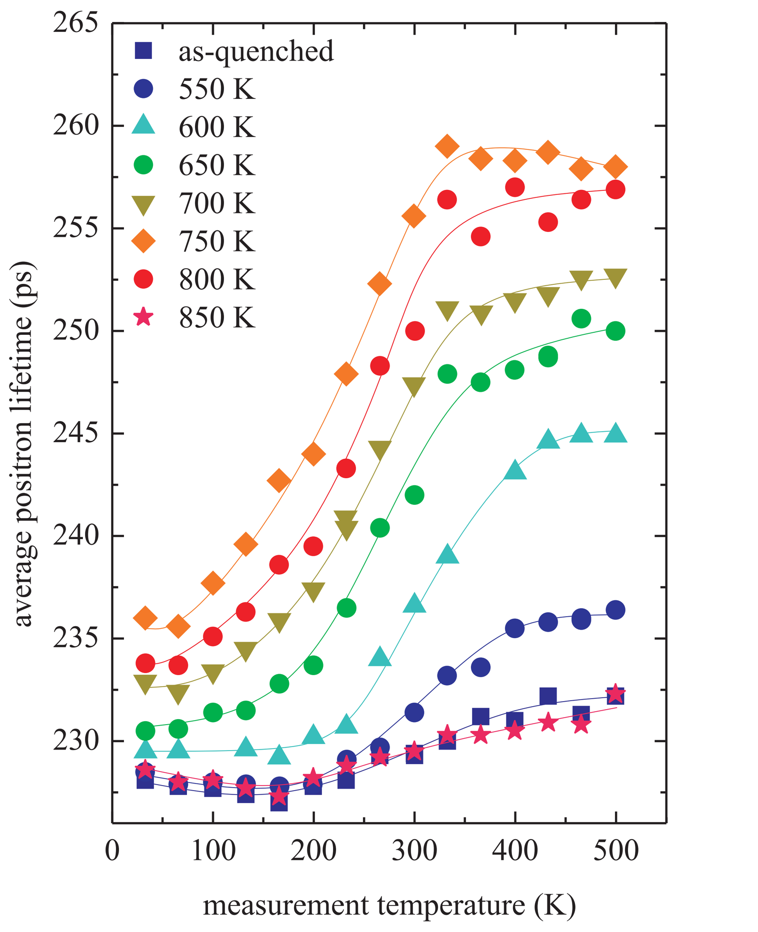

Fig. 2. τ_{av} as a function of sample temperature in SI GaAs. Prior to the experiment, about 6x10^{18} Cu atoms were introduced by evaporating a layer of 30 nm Cu onto the sample surface and by subsequent annealing at 1100 °C under 5.57 bar of As pressure (3h, then quenched into water). The PAL temperature dependence measurements were performed after each annealing step.

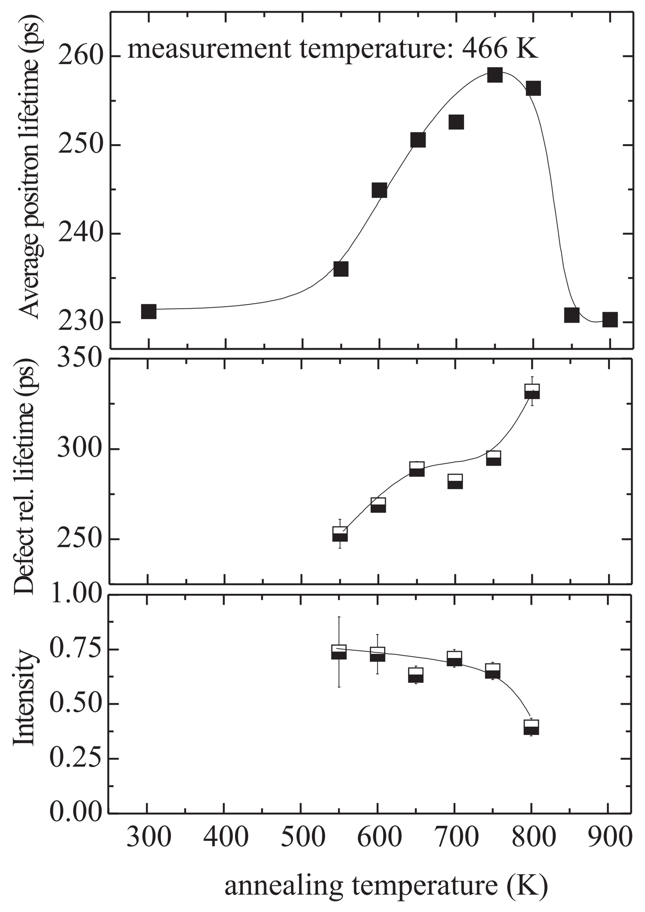

Fig. 3. Positron lifetime results of the annealing experiment of SI GaAs after Cu in-diffusion at 1100 °C under 5.57 bar of As pressure. The average lifetime is shown in the upper panel. The defect-related lifetime and its intensity versus the annealing temperature are plotted in the lower two panels. The spectra were measured at a sample temperature of 466 K to diminish the influence of the shallow traps.

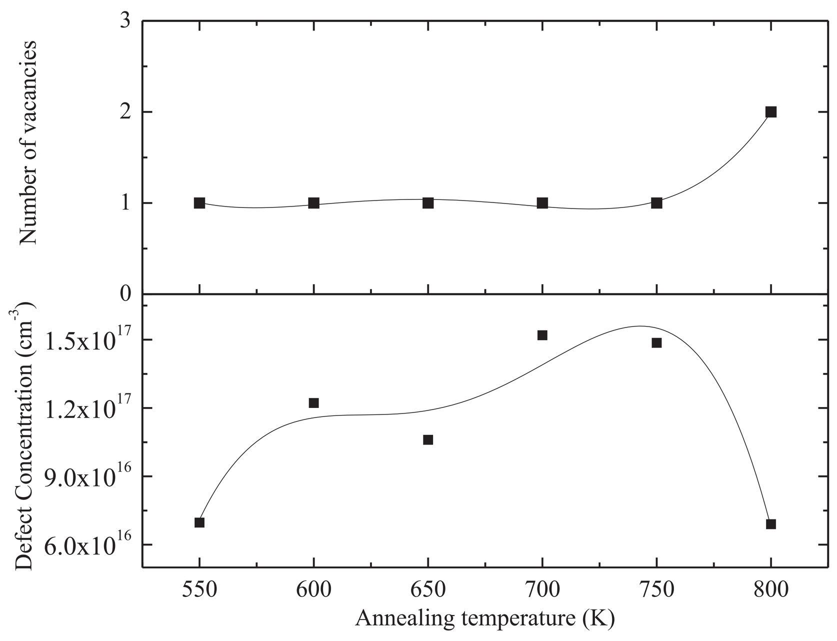

Fig. 4. Defect concentration and the number of vacancies as a function of the annealing temperature in SI GaAs after Cu in-diffusion at 1100 °C under 5.57 bar of As pressure. These Data were calculated using the positron lifetime results presented in Fig. 3.

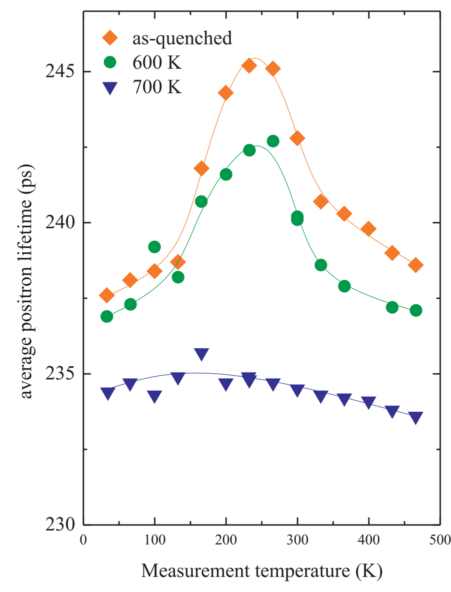

Fig. 5. τ_{av} as a function of sample temperature in SI GaAs. The samples were annealed at 1100 °C under 5.57 bar of As pressure. The samples were not treated with Cu as a reference experiment to the results shown in Fig. 3.

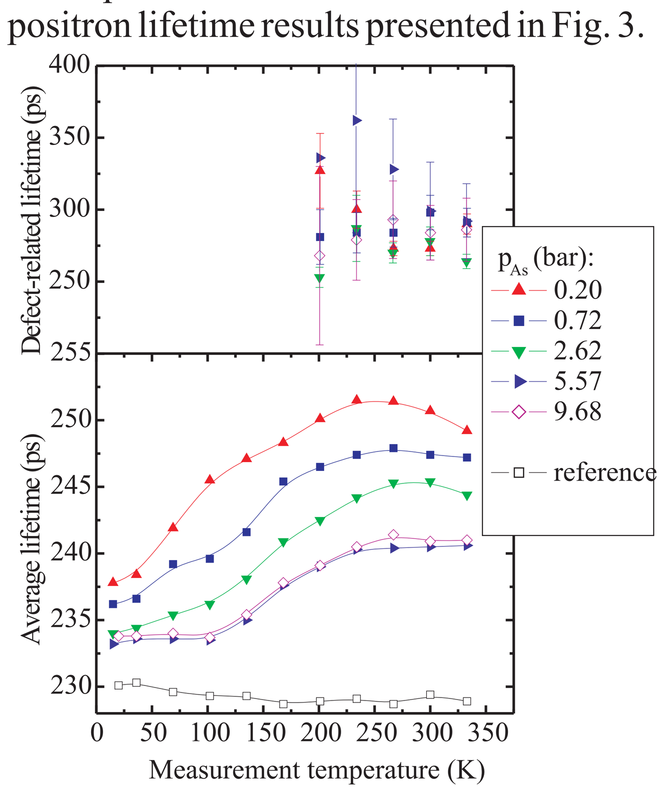

Fig. 6. τ_{av} and τ_d versus measurement temperature for undoped semi-insulating GaAs annealed at 1100 °C for 3 h under different As pressures compared to a not annealed reference sample..

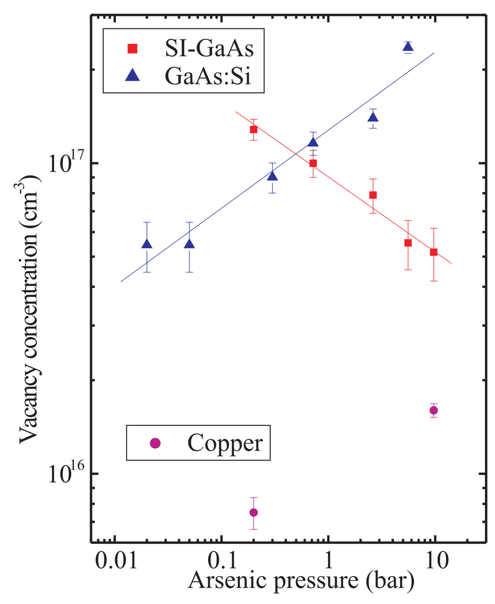

Fig. 7. Vacancy defect concentrations in SI and Si-doped GaAs versus As vapor pressure during annealing at 1100 °C. Solid lines are the power law fits to the data points. Closed circles present the concentration of Cu impurities obtained with the help of titration measurements.

No defects were observed in the SI GaAs reference sample where the average lifetime is close to 230 ps at all measurement temperatures. After annealing the average lifetime is strongly increased (Fig. 6) what proves the generation of vacancy-like defects during the annealing treatment.

With increasing the arsenic vapor pressure (P_{As}) the τ_{av} decreases. The pressure dependence of the τ_{av} reflects an inverse relation between the defect concentration at 1100 °C and the P_{As}.

The value of τ_d at 300 K is 293 ±10 ps (upper panel of Fig.6) what is distinctly higher than the lifetime in Te- and Si-doped GaAs (254 and 262 ps respectively) where V_{Ga} was fond to be responsible for positron trapping. But this value still lies in the region of a monovacancy because the value calculated for a V_{Ga}-V_{As} divacancy defect in GaAs is 332 ps [5].

From the τ_d alone we cannot determine to which sublattice the detected vacancy belongs to. This can be answered by the help of thermodynamic considerations. The vacancy formation in GaAs for Ga and As vacancies as expressed by Eqs. (2) and (3) respectively.

$$1/4As_4^{gas} \quad As_{As} + V_{Ga} . \qquad (2)$$

$$As_{As} \quad V_{As} + 1/4As_4^{gas} . \qquad (3)$$

$$[V_{Ga}] = K_{VGa} \, ' \; P_{As}^{1/4} . \qquad (4)$$

$$[V_{As}] = K_{VAs} \, ' \; P_{As}^{-1/4} . \qquad (5)$$

According to the mass action law, the concentrations of these defects can be derived as expressed in Eqs. (4) and (5). K_{VGa} and K_{VAs} are the mass action constants for Ga and As vacancies at certain temperature. From Eqs. (4) and (5), it is clear that the concentration of V_{Ga} and V_{As} should have an opposite behavior with respect to P_{As} and the V_{As} concentration is inversely proportional to P_{As}.

Fig. 7 reveals an opposite behavior of the concentration of vacancy-like defects with increasing P_{As}. Compared to the data for GaAs:Si. The fits to experimental data represent the power law and yield an exponent close to 0.25 for GaAs:Si and -0.25 for SI GaAs. The vacancy concentration in SI GaAs exhibits an opposite behavior and deacreases with increasing P_{As}.

Hence, the origin of the observed vacancy-like defects in annealed SI GaAs is ascribed to V_{As} but it cannot be the isolated As vacancy.

Hall-effect measurements showed that all investigated annealed samples became slightly p-type with a concentration of [p] = 10^{11}-10^{12} cm^{-3} that corresponds to the position of Fermi level at 0.4-0.5 eV above the valence band. We suppose that we are dealing with a V_{As} defect in complex which is not any more positively charged.

The concentration of Cu impurities for the two samples annealed at 0.2 and 9.68 bar of P_{As} according to titration measurements was about one order of magnitude lower than the measured number of the vacancy-complex. This means that Cu is not a constituent of the observed defect complex.

Summary

During a subsequent annealing up to 750 K after the diffusion treatment (out-diffusion), τ_{av} increases strongly indicating the generation of vacancy-type defects. With a further increase of the annealing temperature to 850 K, a rapid decrease of the average positron lifetime was observed.

The open volume of the detected vacancy-like defect increases during annealing, in contrast to the Semi-insulating undoped GaAs samples annealed under very similar conditions but not treated with Cu.

Vacancy-like defects and shallow positron traps were observed.

It was concluded that the observed vacancy-like defect contains an arsenic monovacancy.

We assumed the presence of a vacancy complex containing an As vacancy and its charge must be neutral or negative in our p-type samples.

We believe that the observed vacancy complex is not bound to Cu impurities and represents a native defect complex. But the structure of the complex cannot be exactly determined from positron annihilation parameters

References

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