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On the Interaction of Copper with Defects in Gallium Arsenide*

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The behavior in gallium arsenide of copper introduced through the melt has been investigated. Measurements have been made on the electrical and photoluminescent properties of single crystals that had either been quenched from T_{cryst}, slowly cooled after crystallization or thermally annealed at 1100°C after completion of the growth. On quenching from T_{cryst}, formation of very shallow acceptors is observed. On slow cooling or annealing at 1100°C, acceptor levels are formed of the order of 0.12 and 0.02 eV. The concentration of carriers for both levels diminishes with lower temperatures of annealing and with concentration of copper added. The 0.12 eV level is assigned to the center $(\text{Cu}_{\text{Ga}}\, V_{\text{Ga}})^-$.

Introduction

The behavior of copper in gallium arsenide has been repeatedly considered in the literature. Diffusion of copper into GaAs by the mechanism of exchange implantation forms a donor level Cu_i^+ at −0.07 eV and an acceptor center $\text{Cu}_{\text{Ga}}^{2-}$ having ionization energies of 0.145 and 0.45 eV (*1–3*). However, thermal conversion of GaAs by impurity copper from quartz gives, in place of the 0.145 eV level, a level at 0.12 eV (*4*). From the magnitude of the diffusion coefficient of the copper in the thermal conversion, the author of Ref. (*4*) concludes that it is necessary to take account of a possible interaction between copper and gallium vacancies. Klotinsh (*5*) found, under certain conditions of copper diffusion, an acceptor level at 0.13 eV. Its formation was explained by interaction of acceptor copper with donor impurities.

Thus, the behavior of copper in gallium arsenide is substantially influenced by either native or other impurity defects. Since copper appears to be one of the principal uncontrolled impurities, resulting from diffusion out of quartz into the crystals on crystal growth, it is of interest to study the behavior of copper when it is deliberately added through the melt. Alloying of copper with gallium arsenide by fusion has been studied intensively by Fuller et al. (*6*). However, they gave major attention to the formation of shallow acceptor level at 0.02 eV.

The purpose of the present communication is to describe a study of the behavior of copper, added to starting melts, as a function of growth conditions and subsequent thermal treatment of the single crystals obtained.

Experimental

Dislocation-free or nearly dislocation-free ($N_d \leqslant$ 50–60 cm^{-2}) single crystals of GaAs were grown from the melt by the method described in (*7*). Alloying impurity was added to the melt in the form of 2% alloy. The compositions of the starting melts ranged from 49.0 to 51.5 at % As. Samples with copper content of about 10^{19} atoms/cm^3 were cooled from T_{cryst} in various ways: (1) quenched from T_{cryst} in air; (2) after completion of growth, cooled slowly *in situ* in the furnace at a rate of 200°/hr; (3) after completion of growth, cooled rapidly to 1200 or 1100°C, then annealed at that temperature, and finally quenched in water.

The cylinder-shaped specimens were cut into disks perpendicular to the axis of growth and then into plates of rectangular shape, on which were performed the electrical measurements by the usual four-probe method. On specimens of small dimensions, the measurement of conductivity was by the method of van der Pauw. Most of the measurements

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were carried out in the temperature range 77–400°K, using indium or tin contacts. Isolated specimens were measured from 20 to 300°K.

The majority of copper-alloyed specimens had two acceptor levels. For such systems the concentration of carriers depends on temperature in the following way:

$$p + N_d = \frac{N_{a_1}}{1 + \beta_1 \frac{p}{N_v} e^{\Delta E_1/kT}} + \frac{N_{a_2}}{1 + \beta_2 \frac{p}{N_v} e^{\Delta E_2/kT}} \qquad (1)$$

All symbols are standard. The parameters N_{a_1}, N_{a_2}, N_d, ΔE_1, and ΔE_2 were determined by computer programming, assuming that $\beta_1 = \beta_2 = 2$, $m^* = 0.5m_0$, $A(r) = 1$. An example of such a calculation is given in Fig. 1. The precision of the calculation of N_{a_2} and ΔE_2, which for us has the greatest interest, was set by the precision of the experiments. For the quantity N_d and, to a lesser extent, for N_{a_1} the precision of the calculation is less, since almost all the measurements were carried out at temperatures higher than 77°C.

Some authors have calculated the compensation coefficient from the temperature dependence of mobility (*8*). We have carried out analogous calculations assuming that

$$\mu_H^{-1} = \mu_i^{-1} + \mu_{ph}^{-1} + \mu_{cl}^{-1}, \qquad (2)$$

where μ_H is the experimental Hall mobility, μ_i is the mobility determined by scattering by charged ions (after Brooks–Herring), μ_{ph} is the mobility determined by optical phonon scattering (after Ehrenreich), and μ_{cl} represents cluster scattering (after Weissberg). In Fig. 2, an example of such a calculation is shown.

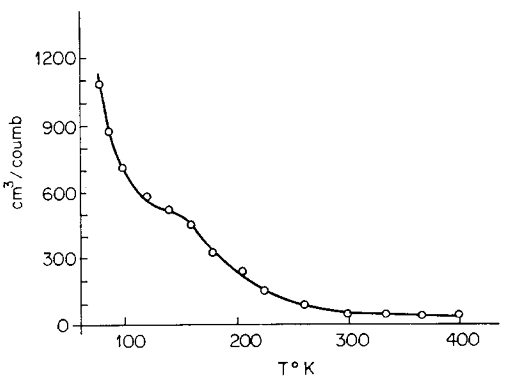

FIG. 1. Temperature dependence of the Hall coefficient R_H. Ordinate is R_H in cm³ coulomb^{-1}; abscissa is T in °K. Solid curve is calculated; points are experimental data.

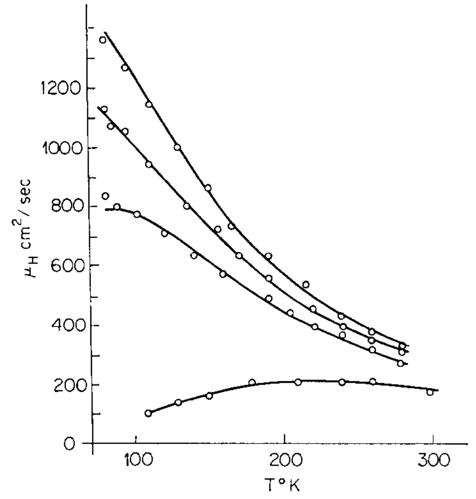

FIG. 2. Temperature dependence of the mobility. Ordinate is μ_H in cm²/V sec; abscissa is T in °K. Solid curves are calculated; points are experimental data.

Results

All the crystals, alloyed with copper in the melt, had *p*-type conductivity. The samples quenched from T_{cryst} had large concentrations (up to 10^{17}–10^{18}/cm³) of shallow acceptor and donor levels ($N_a \approx N_d$).

For the specimens that were slowly cooled in the furnace or annealed at temperatures of 1200° or 1100°C after completion of growth, two acceptor levels with ionization energies $\Delta E_1 = 0.02$ eV and $\Delta E_2 = 0.12$ eV were determined from the temperature dependence of the Hall coefficient. The specimens studied in the greatest detail were annealed at 1100°C for about two hours. The annealing temperature 1100°C corresponds to maximum solubility of copper in GaAs (*11*); the duration of annealing was determined by attainment of constant concentrations of N_{a_1} and N_{a_2} at the temperature 1100°C. Since the amount of copper initially introduced in the crystals (2×10^{19}/cm³) exceeded the copper solubility at 1100°C (6×10^{18}/cm³, according to the data of Ref. (*11*)), there might be anticipated a contribution of metallic conductivity indicating precipitated copper. However, this was not observed, for reasons explained in Ref. (*9*).

To clarify the nature of the acceptor levels produced in the crystals by the alloying copper after annealing at 1100°C, the following studies were carried out:

1. Determination of the dependence of N_{a_1}, N_{a_2}, and N_d on the composition of the starting melt.

2. Determination of the dependence of N_{a_1} and N_{a_2} on the content of copper and of silicon in the crystals.

3. Prolonged consecutive annealing at temperatures of 1000, 800, and 500°C for 5 hr with subsequent quenching in water.

4. Extraction of copper by tin.

1. Figure 3 shows the concentration dependence of acceptors and compensation donors on the composition of the melt, as calculated by the previously described methods. The curves for the concentration dependence of N_{a_1} and N_d, calculated from Eq. (1) (Fig. 3*b*) and from Eq. (2) (Fig. 3*b*), show the maximum characteristic of crystals grown from stoichiometric melts, but the quantity N_d in Fig. 3*a* is considerably lower, especially for the samples grown out of melts with excess arsenic. The discrepancy is attributed to the presence of unknown scattering centers and requires further study. The concentration dependence of N_{a_2}, calculated from Eq. (1) (Fig. 3*a*) has a fairly pronounced maximum for melts containing 50.5–50.6 at % As.

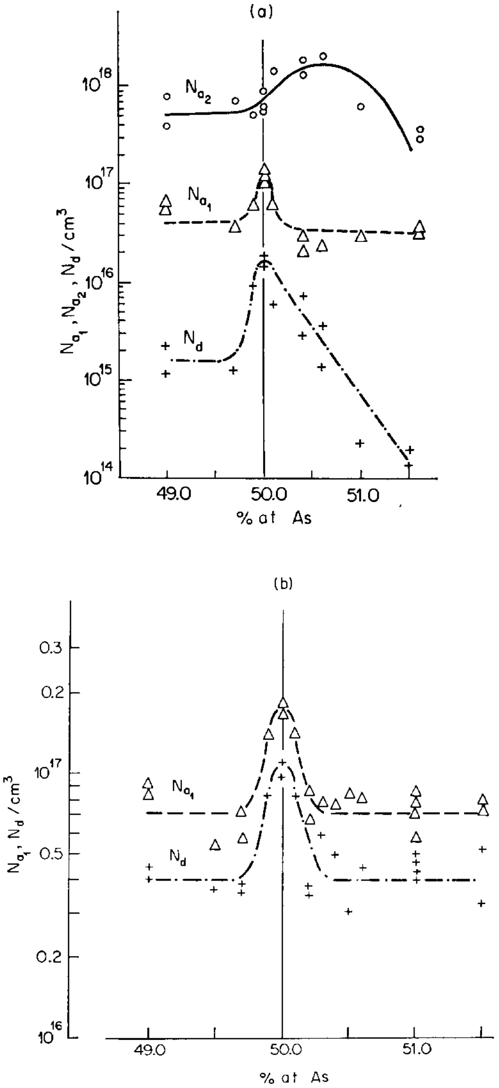

FIG. 3. Dependence of N_{a_1}, N_{a_2}, and N_d on the composition of the starting melt. Ordinate is concentration per cm^3; abscissa is concentration in atomic % arsenic. (*a*) is calculated by Eq. (1); (*b*), by Eq. (2).

2. The concentrations of acceptor levels N_{a_1} and N_{a_2} increase with increase in the copper content of the crystals to limiting values corresponding to saturation (Fig. 4). For N_{a_2}, in the range of copper concentration 10^{17}–10^{18}/cm^3, this dependence is a direct proportion. Simultaneous introduction of copper and silicon to the starting melts raises, in order, the quantities N_{a_1} and N_d at constant N_{a_2}.

3. Successive annealing of the specimens at temperatures of 1000, 800, and 500°C for 5 hr with subsequent quenching sharply lowers N_{a_1} and, to a lesser degree, N_{a_2}. If the annealing is carried out all at once at 500°C, there occurs an abrupt decrease of mobility which is not subsequently restored even after prolonged annealing. Milvidskii et al. (*10*) attribute this phenomenon to structural dislocations and precipitation of a second phase from strongly supersaturated solutions.

4. To extract copper out of the samples, tin was electrolytically deposited on them, after which the samples were annealed at a temperature of 800°C for 50 hr or at 1000°C for 25 hr. In this way, the extraction of copper proceeded to the limits corresponding to the maximum concentration of N_{a_2} at the temperature of extraction.

Figure 5 shows, in curve 1, the temperature dependence of N_{a_2}; in curve 2, the temperature dependence of acceptor concentration formed dur-

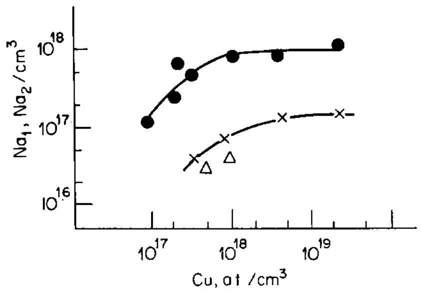

FIG. 4. Dependence of N_{a_1} (shown by *X*) and of N_{a_2} (shown by circles) on the overall copper content in the crystal. Δ represents data from Ref. (6) for N_{a_1}. Abscissa is atoms/cm^3.

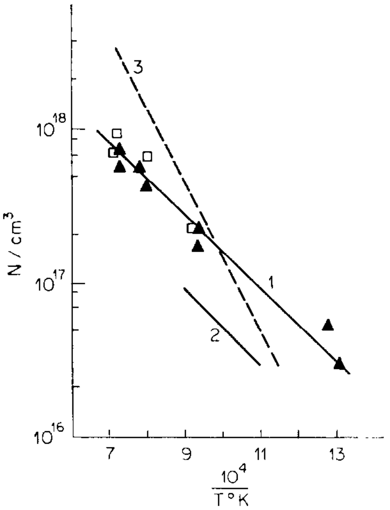

FIG. 5. Curve 1 (filled triangles) gives the dependence of N_{a_2} on annealing temperature. Curve 2 gives the dependence of the concentration of thermal acceptors formed on diffusion of copper out of quartz, according to the data of Ref. (4). Curve 3 gives the solubility of copper in gallium arsenide, according to the data of Ref. (11). The open squares give the residual concentration of copper after extraction with tin. Ordinate is concentration per cm³; abscissa is $10^4/T$(°K).

ing annealing of GaAs by diffusion of copper from the walls of a quartz container (according to the data of Ref. (*4*)); and, in curve 3, the solubility of copper in GaAs (according to the data in Ref. (*11*)). The final values of copper concentration after extraction with tin at 1000° and 800°C agree with the values of N_{a_2} on curve 1.

The photoluminescence spectra of samples alloyed with copper in the melt and annealed at 1100°C always had peaks at 1.48 eV, but they did not show any peaks corresponding to the 0.12 eV acceptor levels found in the Hall measurements. On introduction, by diffusion, of copper into the specimens, a peak appeared at 1.36 eV, provided that the time of diffusion did not exceed 10–30 min. This peak corresponded to the 0.14 eV acceptor level of the R_H measurement. However, when the time of diffusion was increased to a few hours, the 1.36 eV peak disappeared, whereas, by Hall measurements, this corresponded to a conversion of the 0.14 eV acceptor center to 0.12 eV.

Discussion

The absence of an 0.12 eV acceptor center in the specimens as quenched from T_{cryst} and its appearance after annealing at high temperatures (1200°C and lower) shows that it is formed in the crystal only in the process of thermal working on diffusion of copper to lattice sites. To identify the nature of this center, we proceeded from the following facts:

1. The presence of a direct proportionality in the dependence of N_{a_2} on the copper content in the crystal indicates that for every atom of copper introduced there is produced one acceptor center (Fig. 4).
2. From the slope of the curve for the dependence of N_{a_2} on excess arsenic content in the melt, it follows that to each acceptor center there correspond two arsenic atoms in excess (or two gallium vacancies). (Figure 6 gives, for the concentration interval 50.0–50.6 at.% As, the concentration dependence recalculated as atoms per cm³ of excess arsenic in the melt.)

Therefore, the reaction of formation of the complex can be represented in the following way:

$$\text{Cu}_{\text{Ga}}^{-} + (V_{\text{Ga}}V_{\text{Ga}})^0 \rightleftarrows (\text{Cu}_{\text{Ga}}V_{\text{Ga}})^-,$$

$$K = \frac{[(\text{Cu}_{\text{Ga}}V_{\text{Ga}})^-]}{[\text{Cu}_{\text{Ga}}^{-}][(V_{\text{Ga}}V_{\text{Ga}})^0]}$$

i.e.,

$$[(\text{Cu}_{\text{Ga}}V_{\text{Ga}})^-] \propto [(V_{\text{Ga}}V_{\text{Ga}})^0].$$

Participation of a donor center in this reaction through formation of a complex of the type $(\text{Cu}_{\text{Ga}}D_{\text{Ga}})^-$ appears relatively improbable to us for the following reasons:

1. Donor impurities at concentrations of the order of $10^{17}/\text{cm}^3$ might be silicon or oxygen. The great affinity of oxygen to silicon excludes the possibility of its interaction with copper. A complex of the type CuO would be thermally unstable.
2. An increase of silicon concentration in the starting melt essentially does not change the concentration of N_{a_2}.

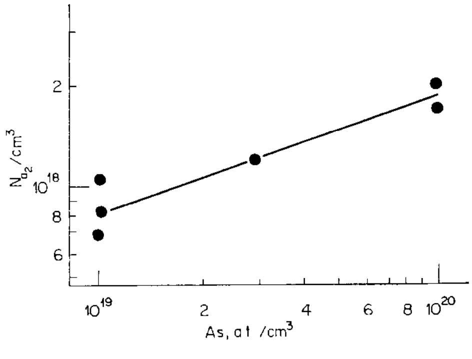

FIG. 6. Dependence of N_{a_2} on the excess arsenic content in the melt (according to the data of Fig. 3*a*). Abscissa is atoms/cm³.

3. On the formation of the combination copper plus donor impurity, the first level of ionization $Cu_{Ga}^{=}$ would be compensated by donors, but the ionization energy of the second level could not be lower than the ionization energy of the first—0.145 eV (*12*).

The formation of a complex of the type $(Cu_{Ga}V_{Ga})^-$ agrees well with experimental facts cited in the literature. Thus, Hwang found disappearance of the 1.36 eV peak in photoluminescence spectra after thermal working at high temperatures (*13*). Transformation of a defect center $Cu_{Ga}^{\equiv}$ into $(Cu_{Ga}V_{Ga})^-$ would lead to the disappearance of the 1.36 eV peak, since the center $(Cu_{Ga}V_{Ga})^-$ is nonradiative.

Fuller et al. (*14*), in their studies of diffusion and extraction of copper in GaAs, attributed the appearance of an acceptor level at 0.1 eV after extraction to formation of gallium vacancies. According to our data, however, the copper is extracted only to the concentration N_{a_2} that corresponds to the temperature of extraction (e.g., $2 \times 10^{17}/cm^3$ at 800°C (Fig. 5)). Since extraction takes place at high temperatures for prolonged periods of time, it leads to the formation of a complex $(Cu_{Ga}V_{Ga})^-$, which is not completely extracted. Because the concentration N_{a_2} decreases with decreasing temperature, the completeness of copper "abstraction" at 600°C must actually be greater, as Fuller noted.

Comparison of the solubility curve of copper in GaAs with the temperature dependence of N_{a_2} (Fig. 5) shows that, in the region of low temperatures (500–700°C), the solubility of copper is considerably increased by complex formation. At temperatures of 800°C and higher, the copper solubility exceeds the concentration of N_{a_2}. It must be that a part of the copper is in the form of other species, Cu_i^+, $Cu_{Ga}^{=}$, or neutral complexes and precipitates.

The sameness of the slopes of curves 1 and 2 (Fig. 5) indicates identity in the nature of the acceptors considered in our work and in Ref. (*4*); the discrepancy in absolute values can be explained by the limitation of the copper source in Ref. (*4*) to amounts insufficient for reaching equilibrium values of N_{a_2}.

A shallow level at 0.02 eV has been observed by several authors in curves of the temperature dependence of R_H and in photoluminescence spectra (*6*, *15*, *16*). The level always appears in the presence of copper, but it has been surmised that it is a simple acceptor such as silicon or carbon (*6*, *14*). For the present, we do not have enough data to say definitely what its nature is; however, we can conclude that it is not a simple center but a complex one, since its appearance and maintenance strongly depend on thermal working. From the fact that the concentration dependence of this level on the composition of the starting melt shows a maximum for the stoichiometric composition, it appears that the complex center must be a result of interaction between impurity atoms on neighboring Ga and As lattice sites, for example $(Si_{Ga}Si_{As})$.

Conclusions

1. The behavior of copper melt introduced in GaAs has been studied. It has been shown that copper interacts with gallium divacancies to form a nonradiative acceptor center $(Cu_{Ga}V_{Ga})^-$ with ionization energy of the order of 0.12 eV.

2. Formation of complexes of the type $(Cu_{Ga}V_{Ga})^-$ increases copper solubility over the temperature interval 500–750°C.

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