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SOLUBILITY AND DISTRIBUTION COEFFICIENT OF CADMIUM IN GALLIUM ARSENIDE

BY MASATOMO FUJIMOTO

From the diffusion profiles the solubilities of cadmium in gallium arsenide have been obtained at the temperature between 800°C and 1,100°C. Assuming ideal liquid solution and regular solid solution, the solubilities and the distribution coefficients of cadmium in gallium arsenide have been calculated as a function of temperature and the T-x phase diagram for the GaAs–Cd system has been constructed at the temperature between 800°C and 1,238°C.

Introduction

For semiconductor devices it is important to investigate the impurity solubilities in solids. Chang and Pearson[1] have determined the solubility of zinc in gallium arsenide over a range of temperature. Thurmond and Struthers[2] have reported the thermodynamic arguments for impurity solubilities in semiconductors. Similar measurements have been made for cadmium in gallium arsenide and are shown in this report.

Experimental Procedure

The detailed experimental techniques have been described in the previous paper[3]. The diffusion profiles of cadmium were obtained by the radioactivation analysis and the solubilities were estimated by extrapolating these diffusion profiles to the surface.

The experimentally measured total solubilities of cadmium are plotted as closed circular points in Fig. 1 with the diffusion temperature as abscissa. For comparison, the data of zinc in gallium arsenide are shown in Fig. 1 as crosses. Since cadmium was diffused without excess arsenic, it may be assumed that the system attained equilibrium near the GaAs-Cd pseudo-binary liquid phase composition. The vapor pressure of arsenic is estimated to be in order of the dissociation pressure of gallium arsenide, which is $10^{-6}\sim10^{-2}$ atm at 800°C$\sim$1,100°C[4].

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1) L. L. Chang and G. L. Pearson, *J. Phys. Chem. Solids*, **25**, 23 (1964)
2) C. D. Thermond, *J. Phys. Chem.*, **57**, 827 (1953)
3) M. Fujimoto, *This Journal*, **40**, 21 (1970)
4) C. D. Thermond, *J. Phys. Chem. Solids*, **26**, 785 (1965)

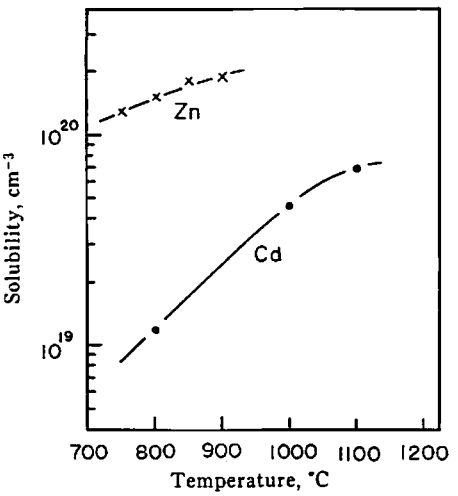

Fig. 1 Solubilities of Zn and Cd in GaAs

Results and Discussions

Assuming that the solid and liquid solutions are regular and ideal, respectively and that the heat of fusion ΔH is independent of temperature, the liquidus line and the distribution coefficient of cadmium are expressed by[5]

$$\ln (1-X_{Cd}^{l}) = \frac{\Delta H_{GaAs}^{f}}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) , \qquad (1)$$

$$\ln k = \ln \frac{X_{Cd}^{s}}{X_{Cd}^{l}} = -\frac{\Delta H_{Cd}^{s} - \Delta H_{Cd}^{f}}{RT} - \frac{\Delta S_{Cd}^{f}}{R} , \qquad (2)$$

where X and k are the atomic fraction and the distribution coefficient, respectively. The superscripts, s and l represent the solid and liquid phase, respectively. ΔH_{Cd}^{s} and ΔH_{Cd}^{f} are the heat of solution and the heat of fusion, while ΔS_{Cd}^{f} is the entropy of fusion of cadmium. T_m is the melting point of gallium arsenide in degree Kelvin.

If it is assumed that all cadmium atoms in liquid phase are neutral, $X_{Cd}^{l}=X_{Cd}^{l^\circ}$, the liquidus line may be calculated from eq. (1) with the known values of ΔH_{GaAs}^{f} and T_m. In solid phase, we assumed that the cadmium atoms exist as either neutral or singly ionized acceptor, $X_{Cd}^{s} = X_{Cd}^{s^\circ} + X_{Cd}^{s^-}$. The distribution coefficients of the neutral cadmium atoms are given by

$$\ln k^\circ = \ln \frac{X_{Cd}^{s^\circ}}{X_{Cd}^{l^\circ}} = \ln \frac{X_{Cd}^{s^\circ}}{X_{Cd}^{l}} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} , \qquad (3)$$

where ΔH is the transfer energy of one mole of the neutral cadmium atom from the liquid to the solid phase and ΔS is the entropy change for this process. From eqs. (2) and (3), the ratio of k° to k is given by

$$\frac{k^\circ}{k} = \frac{X_{Cd}^{s^\circ}}{X_{Cd}^{s}} = \frac{C^\circ}{C} , \qquad (4)$$

5) K. Lehoves, *J. Phys. Chem. Solids*, **23**, 695 (1962)

where C and C^0 are the concentrations of the total cadmium atoms and those of the neutral ones, respectively. The ratio k^0/k can be calculated from the neutrality condition and Fermi energy.

$$C^- + n = p\,, \tag{5}$$

$$C^-/C = \{1 + 2\exp(-\eta_F - \eta_G)\}^{-1}\,, \tag{6}$$

$$n = N_c(2/\sqrt{\pi})F_{1/2}(\eta_F)\,, \tag{7}$$

$$p = N_v(2/\sqrt{\pi})F_{1/2}(-\eta_F - \eta_G)\,, \tag{8}$$

where C^- is the concentration of singly ionized cadmium atoms, n and p are the concentrations of electrons and holes, η_G and η_F are the electronic energy of the valence band and Fermi level. N_v and N_c are the state density of valence and conduction band. $F_{1/2}(x)$ is the Fermi-Dirac function.

At the melting point the surface concentration of cadmium atom is much smaller than the intrinsic carrier concentration n_i. Then, the distribution coefficient of the total cadmium atom k_m is approximated from eqs. (4)~(8) to be

$$k_m = \left(1 + \frac{N_v}{2n_i}\right) k_m^0\,. \tag{9}$$

The experimentally determined solubilities are the total cadmium, while the neutral cadmium atoms are obtained by the theoretical treatments. Then we calculated the solubilities of the neutral cadmium from the experimental data with aid of eqs. (5)~(9) and the distribution coefficients of the total and neutral cadmium atoms at the diffusion temperature were estimated from the liquidus line of eq. (1).

The liquidus line of the GaAs-Cd system is shown on the left in Fig. 2. The liquidus line was

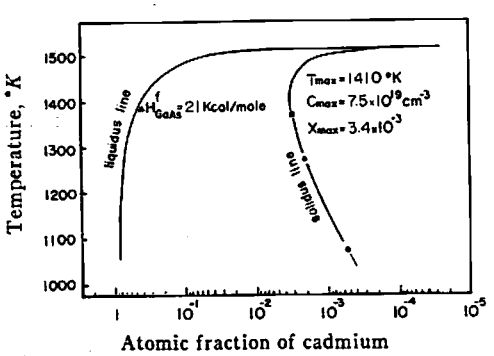

Fig. 2 T–x phase diagram of Cd-GaAs system

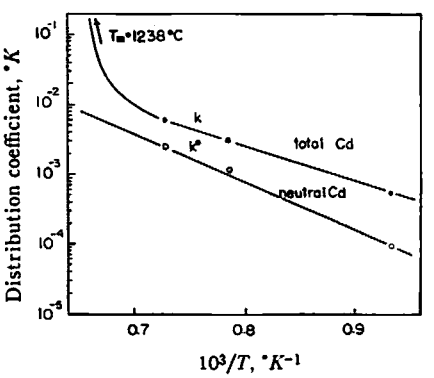

Fig. 3 Distribution coefficient of Cd in GaAs
● : Data points of total Cd calculated from the experimental solubilities and theoretical liquidus line
○ : Neutral Cd calculated from the solubilities of neutral Cd and liquidus line

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calculated from eq. (1), with the following values,

$$\Delta H_{GaAs}^{f} = 21 \text{ kcal/mole}^{6)},\ T_m = 1{,}511°\text{K}. \tag{10}$$

In carrying out the estimations of the neutral cadmium, we used the following values for the energy gap and the effective mass of gallium arsenide[7],

$$E_g = 1.53 - 4.9\times10^{-4}T,$$
$$m_p/m_e = 0.71,\quad m_n/m_e = 0.072. \tag{11}$$

In Fig. 3, the distribution coefficient of the neutral cadmium atom is shown as a function of temperature. In Table 1 the transfer energy, entropy change and melting point distribution coefficient of neutral cadmium are summarized.

Table 1 Transfer energy, entropy change and melting point distribution coefficient of neutral Cd in GaAs

ΔH, kcal/mole	ΔS, cal/mole·deg	k_m°
31.5	11.1	7.3×10^{-3}

The solubilities and distribution coefficients of the total cadmium atom over the whole temperature range can be calculated from the relation of $k^\circ\sim1/T$ in Fig. 3 with eqs. (4)~(8). The calculated results are shown in Fig. 3 as closed circles and the phase diagram are plotted on the right in Fig. 2. The melting point distribution coefficient of the total cadmium is estimated from eq. (9) with the value of k_m° and the temperature of the maximum solubility is obtained from Fig. 2. The results are summarized in Table 2.

Table 2 Maximum solubility, temperature at maximum solubitliy and melting point distribution coefficient of Cd in GaAs

C_{max}, cm^{-3}	T_{max}, °C	k_m
7.5×10^{19}	1137	0.43

Effect of Cadmium Vapor Pressure

The process of dissolving process of cadmium atoms into gallium arsenide under thermal equilibrium is given by

$$Cd(g) + V_{Ga} = Cd^\circ(s), \tag{12}$$

where Cd(g), Cd°(s) are the cadmium atoms in gas phase and in solid phase, respectively.

Applying the mass action law to eq. (12), one obtains

$$[Cd^\circ] = K_1 P_{Cd}[V_{Ga}], \tag{13}$$

6) D. Richman and E. F. Hockings, *J. Electrochem. Soc.*, **112**, 461 (1965)
7) H. Ehrenreich, *Phys. Rev.*, **120**, 1951 (1960)

where [Cd°] is the concentration of the neutral cadmium in solid phase. Since the concentration of gallium vacancy is inversely proportional to the gallium vapor pressure, eq. (13) can be written by

$$[\mathrm{Cd}^{\circ}] = K_2 P_{\mathrm{Cd}} / P_{\mathrm{Ga}} . \qquad (14)$$

In Fig. 4 the solubility of the total cadmium atom at 1,000°C is plotted as a function of the amounts of the added cadmium. The solubility of neutral cadmium atom can be calculated by the similar method as described above. The results are shown in Fig. 4 as open circles.

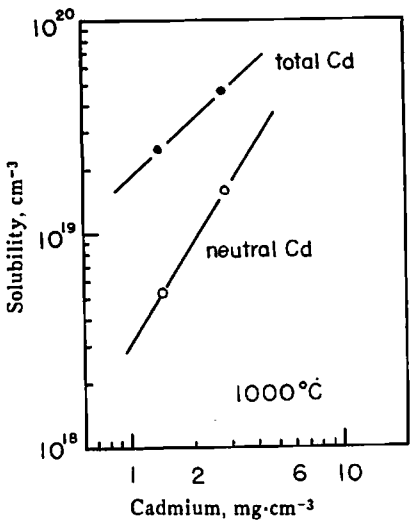

Fig. 4 Solubility of Cd *vs* amounts of added Cd at 1,000°C
● : Data points of total Cd
○ : Calculated solubilities of neutral Cd

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Electrical Communication Laboratory,
Musashino-shi, Tokyo, Japan