

# Formation of p<sup>+</sup>-Layer in GaAs Using the Open-Tube Diffusion of Zn

(Open-Tube에서 Zn 확산을 이용한 GaAs에의 p<sup>+</sup>층 형성)

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## 要 約

Open-tube 확산을 이용하여 Zn의 확산특성 및 그 응용가능성에 대해 연구하였다. 확산원으로써 Ga : poly-GaAs : Zn을 사용하여 GaAs 표면에서 As의 열분해를 방지하였다. Junction의 깊이는  $4.6 \times 10^7 \cdot \sqrt{t} \cdot \exp(-1.25/kT)$ 로 얻어져, 확산의 활성화 에너지는 1.25eV이었다.

Zn의 확산계수는 kick-out model에 잘 일치함을 boltzmann-matano 분석으로 확인할 수 있었다. 확산으로 형성한 p<sup>+</sup>-n 다이오드의 ideality factor는 1.6이었으며, 적외선 강도는 전류에 따라 선형적으로 60배까지 변하였다. 이러한 일련의 결과는 Zn 확산이 kick-out model에 따른 다른 점과 화합물 반도체 소자에 응용 가능함을 보였다.

## Abstracts

Zinc diffusion characteristics and its applicabilities have been studied using an open-tube system. Thermal decomposition of arsenide (As) at gallium arsenide (GaAs) wafer surface was well inhibited by using Ga: poly-GaAs: Zn composition as a diffusion source. Junction depth was obtained as  $4.6 \times 10^7 \sqrt{t} \exp(-1.25/kT)$  where activation energy of diffusion was 1.25eV.

From Boltzmann-matano analysis, it could be identified that concentration dependencies of Zn diffusivity well consisted with those of kick-out model. The ideality factor of p<sup>+</sup>-n junction formed by Zn diffusion was about 1.6 and infrared light intensity was linearly varied in the range of sixty folds. It is concluded from these results that Zn diffuses according to kick-out model, and open-tube method is applicable to compound semiconductor devices.

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## I. Introduction

Zn diffusion is one of the essential processes for the fabrication of p<sup>+</sup>-n junction in GaAs related compound semiconductors. Many authors<sup>(1)(2)</sup> have studied on the applications of Zn diffusion such as ohmic contact, Laser Diode (LD) and

superlattice. For the successful device processing, Zn diffusion techniques have been improved and the diffusion mechanism has been more and more investigated.

In 1960, by Cunell and Gooch, it was reported that diffusion characteristics of Zn in GaAs was anomalous.<sup>(3)</sup> Two years later, interstitial & substitutional model was presented by Longini.<sup>(4)</sup> And Gösele et al.<sup>(5)</sup> improved the model by applying kick-out model in 1981. Recently, it was shown that kick-out model was reasonable in case of closed-tube method from the numerical simulations and the experiments<sup>(6)</sup>. However a few works on open-tube method were reported yet.<sup>(7) (8)</sup>

A work on open-tube diffusion method using graphite boat with diffusion source has been done in our laboratory. This report attempts to define Zn diffusion mechanism in case of open-tube diffusion method, and to cover the basic investigations on the diffused layer by examining electrical properties.

## II. Experiments

Open-tube system was consisted of gas control part, gold furnace and graphite boat as shown in Fig.1. Graphite boat which was designed in order to insert diffusion source and GaAs wafer was - after mechanical processing - precisely rinsed in organic solvents and soaked in 3 HCl: 1 HNO<sub>3</sub> solution for a few hours. N-type GaAs ( $\cong 10^{18} \text{ cm}^{-3}$ ) wafers grown by Horizontal-Bridgeman (HB) method were cleaned with deionized (DI) water and were etched in 3H<sub>2</sub>SO<sub>4</sub>: 1H<sub>2</sub>O<sub>2</sub>: 1H<sub>2</sub>O solution to remove surface contaminants such as oxides. Elements used for diffusion sources were actually very pure materials running about 6 nine grade. The furnace tube was purged for 30 minutes with argon gas, and then forming gas (Ar with 20% H<sub>2</sub>) atmosphere was maintained during heat treatment to prohibit oxidation of the diffusion source and graphite. Gold furnace was movable along the quartz tube so that the heating - and the cooling-rate could be controlled as high as 26°C/min and -40°C/min, respectively.

Zn concentration profiles were obtained by converting the resistivities which were measured by repeating etch-and-measurement with 3H<sub>2</sub>SO<sub>4</sub>: 1H<sub>2</sub>O<sub>2</sub>: 1H<sub>2</sub>O solution. The etch rate was 750Å per 10 sec at 0°C and the measured resistances

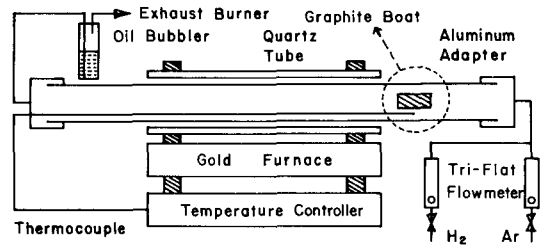


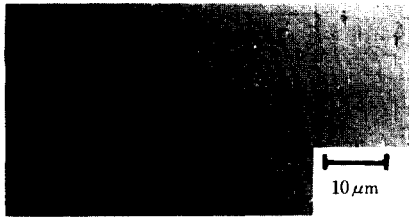
Fig.1. Schematic diagram of open-tube diffusion system.

were converted to resistivities and to Zn concentrations sequentially. Junction depth could be determined not only from Zn concentration profile but also from delineation etching. To delineate p-n junction of GaAs, the cleavage planes of (110) family were etched with 1HF:3HNO<sub>3</sub>: 4H<sub>2</sub>O solution for 10 sec at room temperature (RT). Hall effect measurements were performed using the Van der Pauw method to determine Hall mobility and carrier concentration of the diffused layer. To measure current - voltage (I-V) and light-current (L-I) characteristics, Ohmic contact was made using Indium metal and was baked at 450°C for 2 minutes in flowing nitrogen gas. Light intensity was measured by using SR3000 Light Emitting Diode (LED) tester having silicon (Si) detector.

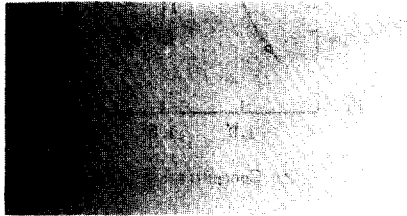
## III. Results and Discussions

### 1. Diffusion Characteristics

Two types of diffusion sources were tried to prevent As from decomposing at GaAs wafer surface during heat treatment. In one diffusion source of As: Zn (50:50 wt. %), As atoms of source ran out so fast that As evaporation was severely occurred at the GaAs wafer surface as shown in Fig.2(a). As can be seen in this figure, rectangular type pits exist to the direction of (110) family on the wafer surface and their feature are V-groove with four planes of (110) family.<sup>(11)</sup> On the contrary, the other diffusion source, Ga:poly-GaAs; Zn (50:25:25 wt%) well suppressed As decomposition and resulted in a clean surface as shown in Fig.2(b). It seems that liquid phase Ga continuously offered to produce As atoms during heat treatments.



(a)



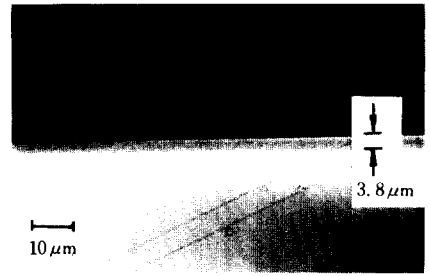
(b)

**Fig.2.** Surface morphologies of Zn-doped GaAs wafers diffused for 400 minutes (a) at 575 °C using Zn: As source and (b) at 600 °C using Ga: poly-GaAs: Zn source.

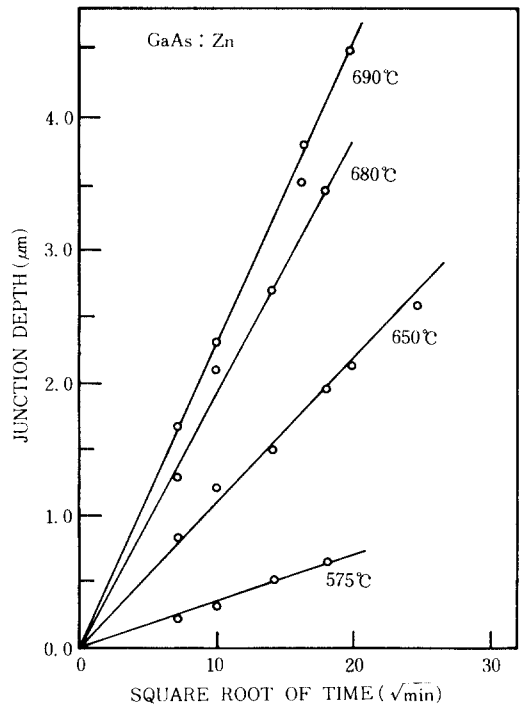
As mentioned above in the experiments, junction depth could be measured by using two methods. Fig.3 shows the delineated p<sup>+</sup>-n junction which was about 3.8μm, however this technique is ambiguous as the junction depth became less than one micron. Therefore most of junction depths were determined from Zn concentration profiles. From the relationship of junction depth with the square root of diffusion time, shown in Fig.4, an experimental result of junction depth which was associated with diffusion - temperature and - time could be represented by the empirical form;

$$d = 4.6 \times 10^7 \cdot \sqrt{t(\text{min.})} \cdot \exp\left(-\frac{1.25}{kT}\right) \quad (1)$$

where d means junction depth in micron and T diffusion temperature in Kelvin degree. The activation energy is almost the same as those reported by Matsumoto<sup>(12)</sup> and Casey<sup>(13)</sup>, as Fig.5, from experiments using closed tube method. The small difference is thought to be occurred from the fact that diffusion coefficient is proportional to P<sub>As</sub><sup>-1/2</sup> and may also be influenced by the source component and atmosphere.



**Fig.3.** Microphotograph of cleavage plane of GaAs wafer delineated by etching.



**Fig.4.** Junction depth vs. square root of diffusion time for various diffusion temperatures.

Maximum Zn concentrations at the wafer surface diffused at several diffusion temperatures between 575°C and 690°C was 1x10<sup>20</sup> - 2x10<sup>20</sup> cm<sup>-3</sup>. As an example, Fig.6 shows that junctions are abruptly formed. Zn diffusion coefficient as shown in Fig.7 was obtained from this figure by using boltzmann-matano analysis which had been

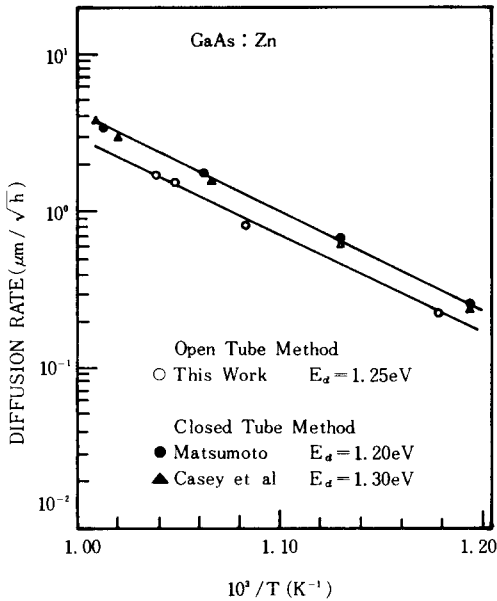


Fig. 5. Diffusion rate (junction depth/diffusion time) vs. reciprocal value of diffusion temperature.

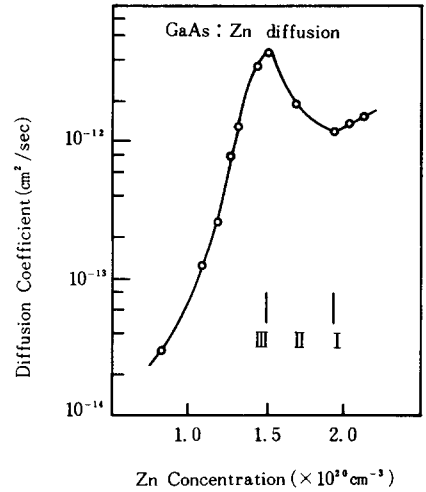


Fig. 7. Diffusion coefficient vs. Zn concentration in GaAs diffused for 40 minutes at 650 °C.

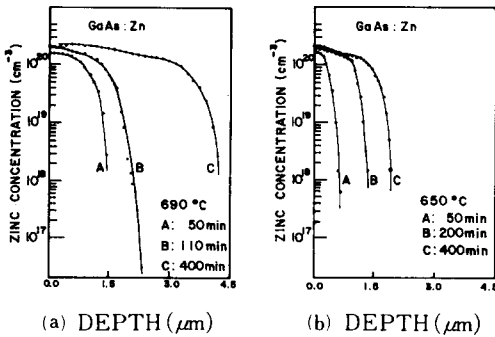
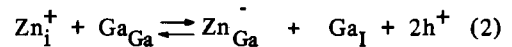


Fig. 6. Zn concentration profiles measured for various diffusion time and temperatures.

known to be useful to study diffusion mechanism depending on impurity concentration.<sup>(14)</sup> Three zone behaviors called anomalous phenomena could be identified through the diffusivity curves as shown in Fig. 7. According to the kick-out model proposed by Gösele and Morehead, this anomalous phenomena can be well described. The kick-out model is a modified interstitial-substi-

tutional model and was presented as following reaction;



where interstitial Zn ( $Zn_i^+$ ) substitute for Ga site to be substitutional Zn ( $Zn_{Ga}^-$ ) and  $Ga_{Ga}$  to be interstitial Ga ( $Ga_I$ ). This phenomena can be explained by applying some assumptions such as Fick's second law and mass action law to Eq.(2), as done by Gösele and his companion. At near surface, as vacancy  $Ga(V_{Ga})$  is easily supplied, all species in Eq.(2) are assumed to maintain equilibrium concentration;

$$C_i(Zn_i^+) \cong C_i^{eq}, \quad C_I(Ga_I) \cong C_I^{eq} \quad \text{and}$$

$$C_s(Zn_{Ga}^-) \cong C_s^{eq}$$

Because of these equilibrium status, diffusion in region I satisfies complementary error function. On the other hand, concentration of  $Ga_I$  in region II is assumed to be accumulated above equilibrium so that the concentration of the species are assumed to be in the order  $C_s \gg C_I \gg C_I^{eq}$  and the diffusivity abnormally becomes proportional to  $C^{-4}$ . This behavior of diffusivity coincides on the whole with the experimental data of region II in Fig. 7.

As Zn Concentration decreases in region III, interstitial Zn ( $Zn_i^+$ ) concentration is assumed to decrease. Interstitial Zn concentration ( $C_i$ ) is less than  $C_1^{eq}$  in this region and Zn diffusivity theoretically becomes proportional to  $C^2$ . But the experimental data of region III in Fig.6 shows that the diffusivity is proportional to  $C^5$  and by far depends on concentration rather than the theoretical value. The difference is presumably due to compensation effect which is dominant in the low concentration region. For the reasons stated above, we propose that diffusion of Zn in GaAs using open-tube method follows kick-out model like that using closed-tube method.

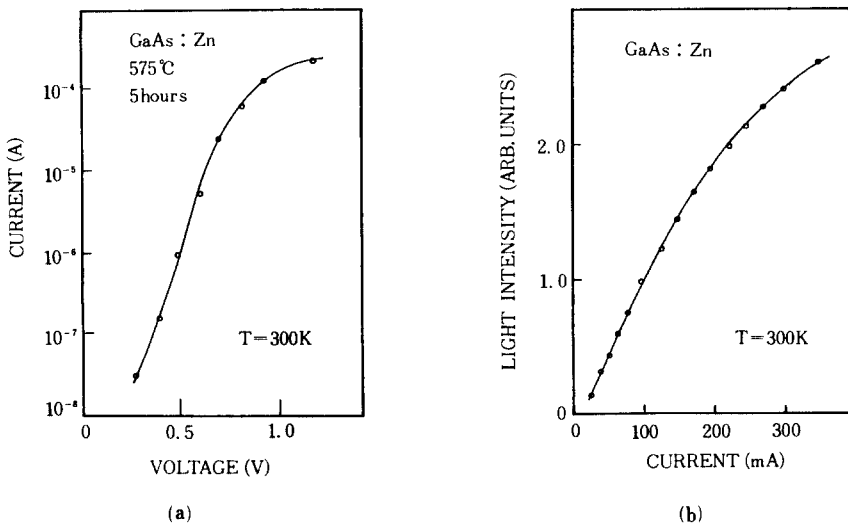
## 2. Electrical Properties

From Hall measurements, the carrier concentrations at surface were measured as  $1 \times 10^{20}$  -  $2 \times 10^{20}$   $cm^{-3}$  and Hall mobilities as 50-70  $cm^2/v.sec.$  The wafer surface was so heavily doped that severely degenerated, and that Hall mobilities were very small.<sup>(15)</sup> The high solid-solubility of Zn in GaAs is the reason that Zn diffusion is useful in ohmic contact.<sup>(16)</sup> The active area of I-V and L-I samples was rectangular type with 2mmx2mm size. The typical relationship of current with forward bias voltage was measured as Fig.8(a).

The ideality factor of junction was 1.6 at low field region. However, as the bias increases above 0.7V, the current becomes to diverge from linearity. This is owing to the series resistance of p-n diode including depletion region. Also soft breakdown was occurred at about 3V because of heavy doping in p-type side of the junction. The wavelength of IR light corresponding to the band gap energy of GaAs emits when the forward bias is applied. The intensity of the IR light was measured to 350 mA at RT as Fig.8(b). The light intensity was linearly increased with current increasing to 200 mA. The divergency occurring above 200 mA is in general caused by the reduction of emission efficiency. The light intensity was linearly increased to sixty orders of magnitude in the arbitrary units as current increased from 10 mA to 200 mA. Therefore, the open-tube method can be applicable to diffuse Zn into GaAs related compound semiconductors and to fabricate optoelectronic devices.

## IV. Summary

One objective of this investigation was to consider Zinc diffusion mechanism in Gallium Arsenide using an open-tube diffusion system. The other objective was to know whether this



**Fig.8.** (a) I-V and (b) L-I characteristics of p-n junction which was formed by diffusion of Zn in n-type GaAs.

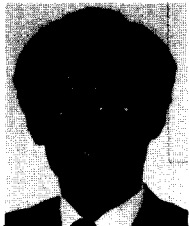
method was applicable to devices needing p-type layer.

The relationship of junction depth with diffusion - temperature and - time was obtained as  $4.6 \times 10^7 \cdot \sqrt{t} \cdot \exp(-1.25/kT)$  where activation energy was 1.25eV. Concentration dependency of Zn diffusivity obtained from experiments showed the same concentration dependencies as approximated from kick-out model: Zn diffusion behavior in the open-tube system could be explained according to kick-out model. The ideality factor of p<sup>+</sup>-n junction formed by Zn diffusion was about 1.6 and IR light intensity was linearly varied in the range of sixty times. In the light of the preceding discussion, open-tube diffusion method must be applicable to compound semiconductor devices.

### Reference

- [1] J.M. Woodall and H.J. Hovel, *Appl. Phys. Lett.* 30, 492, 1977.
- [2] J.W. Lee and W.D. Laidig, *J. Electron. Materials.* 13, 147, 1984.
- [3] F.A. Cunnell and C.H. Gooch, *J. Phys. Chem. Solid.* 15, 127, 1960.
- [4] R.L. Longini, *Solid-State Electronic.* 5, 127, 1962.
- [5] U. Gösele and F. Morehead, *J. Appl. Phys.* 52, 4617, 1981.
- [6] A.H. van Ommen, *ibid.* 54, 5055, 1983.
- [7] S.G. Liu and S.Y. Narayan, *J. Electron. Material.* 13, 187, 1984.
- [8] H.J. Field and S.K. Ghandhi, *J. Electrochem. Soc.* 129, 1567, 1983.
- [9] Y.R. Yuan et al., *J. Appl. Phys.* 54, 6044, 1983.
- [10] L.L. Chang and G.L. Pearson, *ibid.* 35, 1960, 1964.
- [11] Y. Tarui, Y. Komiya, and Y. Harada, *J. Electrochem. Soc.* 118, 768, 1971.
- [12] Y. Matsumoto, *J.J. Appl. Phys.* 22, 829, 1983.
- [13] H.C. Casey et al., *Trans. Metall. Soc. AIME*, 242, 406, 1968.
- [14] J. Crank, "The Mathematics of Diffusion," Clarendon Press, Oxford, 105, 1975.
- [15] Kazuya Masu et al., *J. Appl. Phys.* 51, 1060, 1980.
- [16] H.J. Lee and D.C. Look, *ibid.*, 54, 4446, 1983.

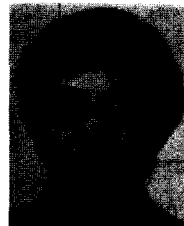
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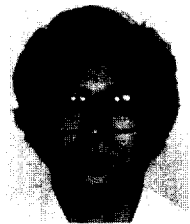
주관심분야는 X-ray 리소그라피, GaAs DIC Process 및 물성분석 Si-EEPROM 개발 소자물리 및 설계 등임.



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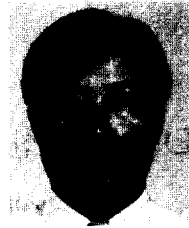
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