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Influences and Kinetics of the GaAs-LPMOCVD Growth Rates Due to Se, Sn, S and Zn Dopants

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This paper deals with LPMOCVD reaction mechanisms and kinetics which explains how ethyle or methyle base plays the different role during growth. Steric hinderence effect for TMG or TEG and static charge effect between Ga-clusters and dopants on the epitaxial layer is proposed. The dopants studied includes TMSn, H_2Se, H_2S and DEZn, as well as DMZn.

A reaction mechanism is proposed as follows

$$As_{As} + V_{Ga}^{-} + p = As_{Ga}^{++} + V_{As}^{+} + 3n.$$

§ 1. Introduction

It is interestingly demonstrated that MOCVD growth rate for GaAs using TMG sources is higher than that of TEG.[1]

By using n-type dopants such as Sn, Se, and S, the growth rate has been enhanced [2,3,4], whereas by using DEZn as dopant, the growth rate is decreased but DMZn reveals the adverse effect [2].

In this report growth reaction mechanism, and growth kinetics are proposed. Theoretical model was subst. antiated by experimental evidences. The experimental system is the asme as previously reported [3].

§ 2. Reaction mechanism

A MOCVD reaction mechanism is proposed as follows,

$$As_{As} + V_{Ga} = As_{Ga} + V_{As}$$

$$V_{Ga} = V_{Ga}^{-} + p$$

$$V_{As} = V_{As}^{+} + n$$

$$As_{Ga} = As_{Ga}^{++} + 2n$$

we obtain,

$$As_{As} + V_{Ga}^{-} + p = As_{Ga}^{++} + V_{As}^{+} + 3n \quad .....(1)$$

This reaction formula pocesses more reasonable deduction than others[5] to explain the origin of EL2, where EL2 is identified as As_{Ga}.

Fig. 1. shows the conversion of conductivity type due to [As]/[Ga] mole ratio, which can be well explained by the formula eqn.(1). As [As]/[Ga] ratio increases, the reaction is push toward right hand side and thus asenic antisite increases and there are more electron (3n) produced.

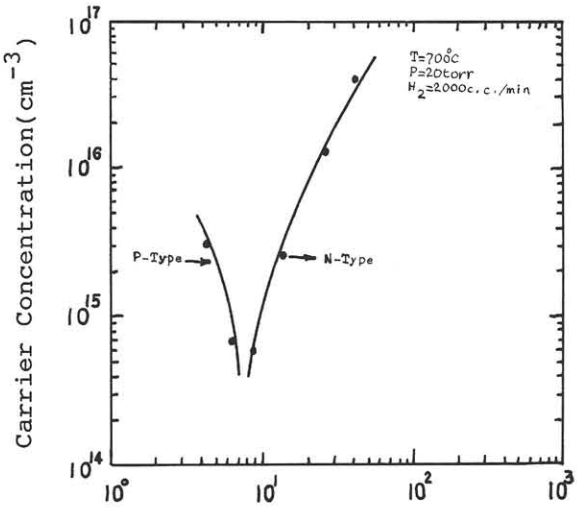

Fig. 1. Effect of the mole ratio of [As]/[Ga] on carrier concentration

§ 3. Influsences of growth rates due to methyle or ethyle based metalorganic sources.

Fig. 2. shows the steric hinderance effect for TMG and TEG. TMG molecule absorbs more heat from substrate thus decomposes more easily than TEG. Therefore the growth rate can be enhanced[3].

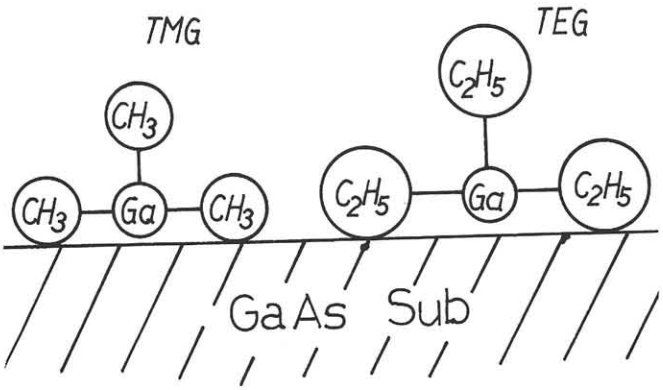

Fig. 2. Steric hinderance effect for TMG and TEG upon GaAs substrate.

§ 4. Growth Rates vs. Dopant Concentration

Systematic studies on the influences of various n-type dopants Sn, Se, S and p-type dopants DEZn and DMZn, Growth rates were obviously altered.

Fig. 3. Shows electrostatic charge effect between Ga-clusters which pocesses slightly positive arround the outer cluster, whereas the ntype dopants pocess slighly negative charges forms a dipole moment. The growth rates were enhanced. It may therefore directly deduced that for p-type dopants, the growth rate would be reduced. For DEZn the prediction may be true, However, For DMZn, it revealed adverse effect may be due to steric hinderance effect as was mentioned in previous section.

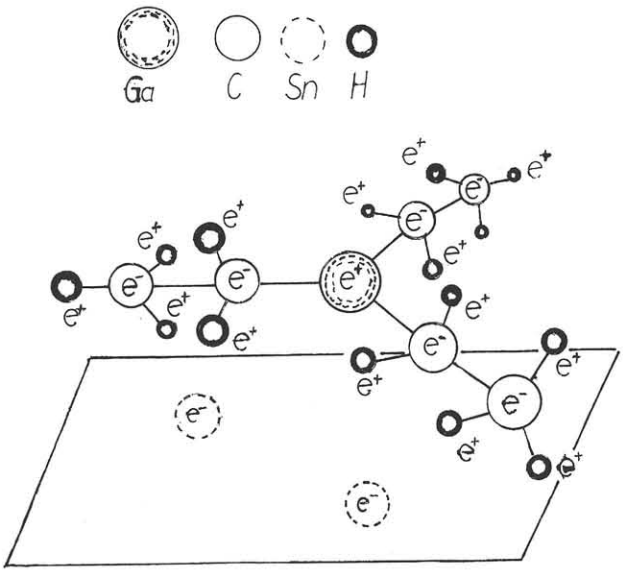

Fig. 3. Electrostatic charge effect due to Ga clusters and dopants.

Fig. 4. shows relative growth rates vs. n type dopant mole fraction. For Se, S, and Sn respectively.

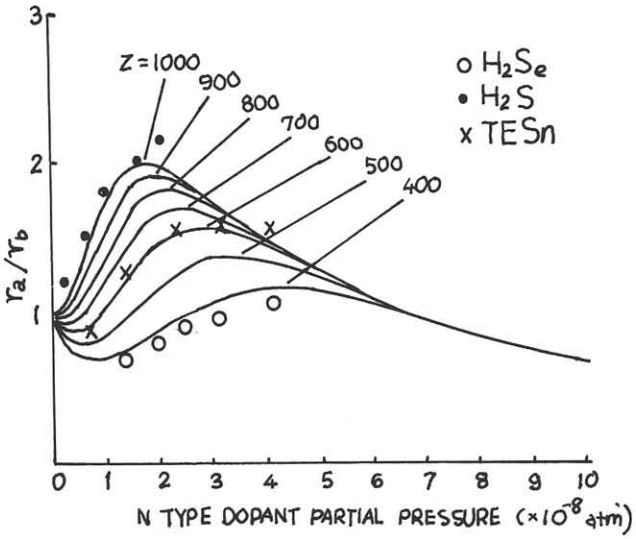

Fig. 4. Relative growth rate vs. ntype dopant partial pressure.

Based on adsorption-desorption model ,growth kinetics has been developed.

The equilibrium adsorption coefficient may be defined as

$$K_1 = \frac{K_{1a}}{K_{1d}} \quad ..[2]$$

where the subscript a stands for adsorption whereas d for desorption.

By considering static charge effect [6], K_1 may be further deduced as

$$K_1 = \frac{B}{1+A\exp(\mp BZP_2)} \quad \cdots\cdots \quad [3]$$

where Z=Columb factor for different dopant.

P_2=dopant's partial pressure.

The growth rate may be deduced as

$$V = \frac{kK_1P_1K_3P_3}{(1+K_1P_1+K_2P_2+K_3P_3)^2} \quad \cdots\cdots \quad [4]$$

where

K_1, P_1=TEG/TMG equilibrium adsorption coefficient and partial pressure.

K_2, P_2=dopant's equilibrium adsorption coefficient and partial pressure.

K_3P_3=AsH_3 equilibrium adsorption coefficient and partial pressure.

The - sign in exponential bracket, for n type dopants, + sign for p type dopants.

Carrier concentration vs. dopant mole fraction is shown in Fig. 5. H_2Se reveals highest doping efficiency, may be due to lower reevaporation rate than H_2S. However TESn reveals different mechanism than these.

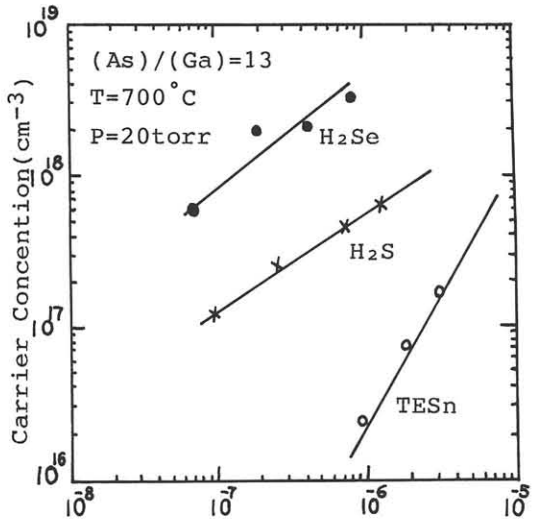

Fig. 5. Carrier concentration vs. ntype dopant mole fraction.

Fig. 6. shows growth rates vs. Zn dopant mole fraction. Growth rate decreases with increasing DEZn concentration, wheras DMZn reveals adverse effect.

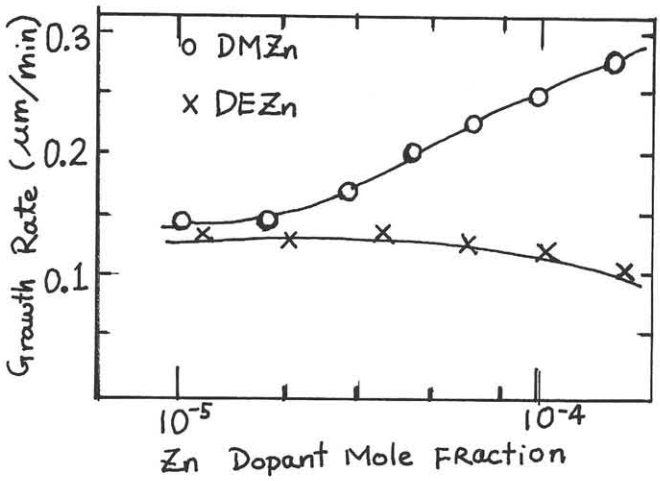

Fig. 6. Growth rate vs. Zn dopant mole fraction.

Fig. 7. shows hole concentration in GaAs vs. DEZn partial pressure with substrate temperature as parameters.

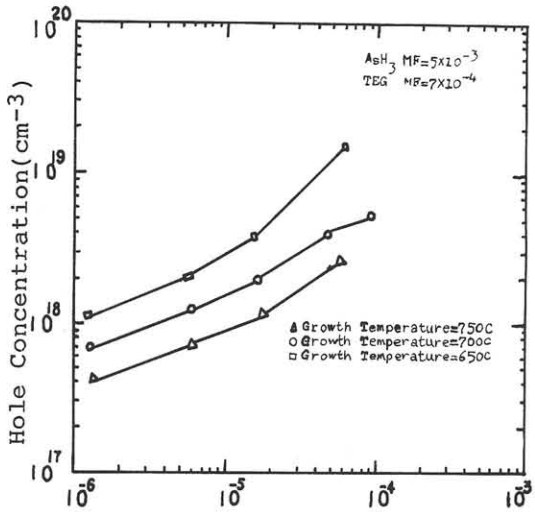

Fig. 7. Hole concentration in GaAs vs. DEZ partial pressure.

§ 5. Conclusions

A growth reaction mechanism has been proposed. A growth kinetics model has been developed which incorporates with steric hinderance effect from TEG or TMG and static charge effects for n type or p type dopants.

A summary is given in table I.

Table I Summary

Dopants	Conductivity type	Enhance(+)/ Dehance(-)
H_2S	n	+
TESn	n	+
H_2Se	n	+
DEZ	p	-
Organic bases		
TMG		+
TEG		—
DEZ	p	-
DMZ	p	+

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