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Modeling GaN Growth by Plasma Assisted MBE in the Presence of Low Mg Flux

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A rate equation model is developed to investigate the plasma assisted MBE growth of GaN in the presence of a fractional monolayer of Mg. Four distinct cases were identified and modeled – (i) Ga-limited regime (ii) Low N-limited regime (iii) Medium N-limited regime and (iv) High N-limited regime. In the model, it is assumed that Ga arriving on a Mg site undergoes faster incorporation into the epilayer through an exchange reaction compared to Ga arriving directly on a N surface. Additionally the incorporation rate of Ga was assumed to depend on the size of the Ga cluster. The results of the model are in good agreement with that of experiments. The non-monotonic behavior of growth rate with Ga flux for moderate Mg coverage is explained based on the incorporation rate dependence of Ga on the cluster size.

1 Introduction

Group III nitrides are important for many opto-electronic devices. The future technologies based on microelectronic devices such as blue light emitting diodes, ultra-violet lasers for high capacity storage devices, and high temperature, high field heterojunction bipolar devices depend on these materials [1]. One method of producing III-nitride based device structures is molecular beam epitaxy. The understanding of the surface kinetics of the growth processes in molecular beam epitaxy is limited despite active experimental research. Thorough understanding of the growth process will help realize reliable production of high quality material in large quantities, which in turn will help in commercializing III-nitride based devices.

In order to make useful solid-state devices, a p-type dopant must be identified. Mg with its thermal activation energy of ~200 meV, is the most suitable candidate at the current level of technology [2]. It is, therefore, important to understand the influence of Mg on the surface kinetics of the GaN MBE growth process. In addition to acting as a p-type dopant, Mg has the benefit of inhibiting Ga droplet formation under N-limited conditions in the MBE growth of GaN [3]. Ga droplets get incorporated into the growing epilayer as pockets of Ga, thus resulting in poorer quality materials [4]. For high Mg fluxes resulting in $^1/_4$ to $^1/_2$ monolayer (ML) surface coverage, the Mg incorporates into the epilayer [2]. However, increasing Mg above 1 ML results in reversal from Ga-polarity surface to N-polarity surface and in lower Mg incorporation [5]. Mg has a much different behavior below $^1/_4$ ML surface coverage. At a low Mg flux, the growth rate increases up to 30% for addition of Mg up to $^1/_4$ ML [3]. Improved growth rates are necessary for producing high yield of material in a short amount of time.

Daudin et al. [3] found three different types of growth behaviors for three different coverages of Mg on the surface (C_{Mg}). When C_{Mg}= 0, the growth rate increases as a function of Ga flux in the Ga limited regime, then saturates at a constant value in the N-limited regime. For C_{Mg}= 0.05 ML, the growth rate increases until a critical Ga flux and then decreases rapidly until another critical Ga flux beyond which it increases and saturates

In spite of several experimental studies on the influence of Mg on GaN crystal quality of growth, the mechanisms of the growth are not well understood. In this article, a rate equation model based on the kinetics of the surface processes is presented (in section 2). In section 3, the results of the model are presented and compared with the experimental data of Daudin et al. [3]. Conclusions of the model are presented in section 4.

2 Model

2.1 Experimental Observations used in the Model

The following experimental results form the basis of the model developed in the study.

i) Mg incorporates into the epilayer for flux values corresponding to a cell temperature of T_{Mg}=250°C and above [2].

ii) GaN growth rate increases with T_{Mg} in the Ga-limited regime of growth with a 30% increase for a change from no Mg present to T_{Mg} =230°C [3].

iii) GaN growth rate reaches a constant value with Ga flux in the N-limited regime for no Mg and T_{Mg} = 230°C with a higher growth rate for T_{Mg} = 230°C [3].

iv) The growth rate decreases drastically in the initial portion of N-limited regime and then increases and reaches a constant value for T_{Mg} =212°C [3].

v) Fewer larger Ga droplets were found in the presence of Mg compared to larger number of smaller Ga droplets when residual Mg was present [3].

vi) Mg segregates to the surface for low Ga coverage cases [6].

vii) Mg increases the surface migration rate of Ga on the surface [2].

viii) Mg on N passivates the N surface, preventing the formation of N-N complexes on the surface [3].

2.2 Theoretical Model

The rate equation model is based on the experimental observations listed in section 2.1 and is similar to the one developed for the GaN MBE growth using Ammonia and ECR N-plasma [7] [8], except that in the present model substrate temperature dependence is not considered. The experimental observations listed in 2.1 necessitate the use of four cases based on the Mg surface coverage.

2.2.1 Case 1: (Ga-limited regime) (C_{Ga}<C_N)

In this case, Ga can arrive on two possible surfaces; Mg or N. The Ga arriving on Mg surface is assumed to undergo a surface exchange mechanism to incorporate into the epilayer, thus allowing Mg to ride to the surface. The Ga will incorporate into the epilayer on the exposed N surface as well. Additionally, evaporation of Ga from the surface was also allowed. Pictorially, these processes are shown in Figure 1a. Mathematically, time evolution of the surface coverage of Ga based on the surface processes can be modeled as:

$$\frac{dC_{Ga}}{dt} = J_{Ga} - \frac{(C_N - C_{Mg})^2 * C_{Ga}}{C_N * \tau_1} - \frac{{C_{Mg}}^2 * C_{Ga}}{C_N * \tau_2} - \frac{C_{Ga}}{t_3} \qquad (1.1)$$

where C_{Ga}, C_{Mg}, and C_N are surface coverages of Ga, Mg and N respectively. C_{Ga} +C_{Mg} in a layer is always less than or equal to 1.0. Anytime that C_{Ga} exceeds 1.0, the excess Ga forms droplets over the layer as shown in Figure 1b. The terms on the R.H.S. describes the change in Ga surface coverage due to Ga flux, incorporation of Ga on the N surface, the incorporation of Ga due to Mg, and the evaporation of Ga, respectively. In the second term, the coverage of N available for Ga to incorporate is $\left(C_N - C_{Mg}\right)$ and the fraction of Ga available for incorporation through direct incorporation is $\left(\frac{C_N - C_{Mg}}{C_N}\right) * C_{Ga}$. In the third term, the available surface to incorporate through the Mg is C_{Mg} and the fraction of Ga available to incorporate through Mg is $\frac{C_{Mg}}{C_N} * \left(C_{Ga}\right)$.

At the steady state $\frac{dC_{Ga}}{dt}$ is equal to zero. Solving for C_{Ga}, we get:

$$C_{Ga} = \frac{J_{Ga}}{\frac{(C_N - C_{Mg})^2}{C_N * \tau_1} + \frac{C_{MG}^2}{C_N * \tau_2} + \frac{1}{\tau_3}} \qquad (1.2)$$

From Equation (1.2) the growth rate is:

$$G = C_{Ga} * \left(\frac{(C_N - C_{Mg})^2}{\tau_1 * C_N} + \frac{C_{Mg}^2}{\tau_2 * C_N}\right) \qquad (1.3)$$

2.2.2 Case 2:(Low N-limited regime) C_{Ga} > C_N and (C_{Ga} –C_N) < C_{Mg}

Case 2 occurs when the Ga coverage exceeds the N coverage by a small value. In this case, there is excess Ga on the surface as shown in Figure 1b. Since, experimentally it is known that Mg causes Ga agglomeration, it is assumed that the excess Ga agglomerates only on the Mg sites. Thus on the Mg sites, a second layer of Ga fills partially on top of the first Ga layer. In the model, it is assumed that due to buildup of two layers of Ga, exchange of the two-layer portion of Ga with Mg is prevented due to Ga-Ga bonding. Thus, as Ga arrives in excess, the second layer coverage of Ga increases and the Mg-Ga exchange decreases and thus, decreasing the overall GaN growth rate. Mathematically, these observations can be modeled in terms of the time evolution of Ga as:

$$\frac{dC_{Ga}}{dt} = J_{Ga} - \frac{(C_N - C_{Mg})^2}{\tau_1} - \frac{(C_{MG} - (C_{Ga} - C_N))^2}{\tau_2} - \frac{C_N}{\tau_3} - \frac{(C_{Ga} - C_N)*C_{Mg}}{\tau_4} \quad (2.1)$$

The terms on the R.H.S. represent the coverage change due to Ga flux, the incorporation of Ga onto the N surface, the incorporation of Ga through the Ga-Mg exchange, Ga evaporation, and Ga droplet formation, respectively. At steady state, C_{Ga} can be obtained as:

$$C_{Ga} = C_N + [\frac{\tau_2}{2} * [(\frac{C_{Mg}}{\tau_4} - \frac{2 * C_{Mg}}{\tau_2}) - \sqrt{(\frac{C_{Mg}}{\tau_4} - \frac{2 * C_{Mg}}{\tau_2}) - [4(\frac{1}{\tau_2})(\frac{C_{Mg}}{\tau_2} + \frac{C_N}{\tau_3} + \frac{(C_N - C_{Mg})^2}{\tau_1} - J_{Ga}]} \quad (2.2)$$

From Equation (2.2), the growth rate equation is obtained as:

$$G = \frac{(C_N - C_{Mg})^2}{\tau_1} + \frac{[C_{Mg} - (C_{Ga} - C_N)]^2}{\tau_2} \quad (2.3)$$

(2.3)

2.2.3 Case 3: (Medium N-limited):($C_{Ga} > C_N$) and ($C_{Ga} – C_N) > C_{Mg}$))

Case 3 occurs when C_{Ga} exceeds ($C_N + C_{Mg}$). In this case, the excess Ga produces a strain on the epilayer that forces the Mg to segregate to the surface. Two competing processes exist according to the site of arrival of Ga, either on top of Mg or on top of Ga droplets, as depicted in Figure 1c. The incorporation of Ga into the epilayer by Mg occurs at a faster rate than Ga incorporating into the droplets. Mathematically, the rate equation for C_{Ga} is:

$$\frac{dC_{Ga}}{dt} = J_{Ga} - \frac{(C_N - C_{Mg})^2}{\tau_1} - \frac{(C_{Mg} - (C_{Ga} - C_N))^2}{\tau_2} - \frac{C_N}{\tau_3} - \frac{C_{Mg}^{\ 2}}{\tau_4} \quad (3.1)$$

Equation (3.1) is similar to Equation (2.1) except that in this case $C_{Ga} – C_N = C_{Mg}$, which physically means that the droplet formation occurs only over the area occupied by Mg.

Under steady-state,

$$C_{Ga} = C_N + C_{Mg} + \tau_2 * \sqrt{J_{Ga} - \frac{C_N}{\tau_3} - \frac{C_{Mg}^{\ 2}}{\tau_4} - \frac{(C_N - C_{Mg})^2}{\tau_1}} \quad (3.2)$$

The growth rate is, G, is given by:

$$G = \frac{(C_N - C_{Mg})^2}{\tau_1} + \frac{(C_{Mg} - (C_{Ga} - C_N))^2}{\tau_2} \quad (3.3)$$

2.2.4 Case 4: (High N-limited) $C_{Ga} > C_N + 2C_{Mg}$

In this case, the Ga droplet on top of the Mg layer completely separates out leaving a Mg layer completely covered with a single Ga layer all the time. All excess Ga agglomerates with the already existing Ga droplet or evaporates. These processes are pictorially shown in Figure 1d. Mathematically, the growth rate is dependent only on C_N and C_{Mg} and is given by:

$$G = \frac{(C_N - C_{Mg})^2}{\tau_1} + \frac{C_{Mg}^2}{\tau_2} \quad (4.1)$$

where the terms on the R.H.S. describes contributions to the growth rate due to the incorporation of Ga on N, and the incorporation of Ga through the Ga-Mg exchange, respectively.

Equations 1.1-4.1 were programmed in C++ language and the computation of G as a function of Ga flux and Mg coverage were performed on a computer with a 450 MHz AMD K6-2 processor.

Growth Rate given by Eqn. 1.3-2.3 (Case 1 and Case 2), Eqn 2.3 -3.3 (Case 2 and Case 3), and Eqn. 3.3-4.1 (Case 3 and Case 4), are equal at Case 1-2, Case 2-3, Case 3-4 limits, respectively.

3 Results and Discussion

The relationship between Ga flux in ML/s and the Ga cell temperature, T_{Ga}, was obtained by comparing the data of Figure 1 of Ref. [9] and Figure 6.(a) of Ref. [3]. Thus, the experimental growth rate, G, versus T_{Ga} data of Ref. [9] can be converted to growth rate, G, versus Ga flux, J_{Ga}. Similarly a quantitative relationship between the magnesium cell temperature, T_{Mg}, and coverage of the surface riding Mg, C_{Mg}, was established using experimental data of Daudin et al. [3] and used in the model. The model parameters, time constants for the various mechanisms, τ_2, τ_3, and τ_4, were found to be dependent on the C_{Mg} by fitting the experimental data with that of our results. The dependence of the time constants on the C_{Mg} is presented in Table . In general, τ_1, τ_2, and τ_4 decreased as C_{Mg} increased, τ_3 increased with C_{Mg}.

The growth rate, G, versus Ga flux, for the case of no Mg present was obtained using Equations 1.2-1.3 and is shown in Figure 2 along with the experimental data. For all growth vs. Ga flux curves several data points were computed for each case. But for purposes of clarity only the growth curve is shown. The agreement between the results is excellent. The growth rate increases linearly with the J_{Ga} in the Ga limited regime and saturates at a constant value in the N-limited regime as expected. The saturation growth rate corresponds to a sticking coefficient of 0.805.

For the cases of residual Mg and T_{Mg} equal to 212°C, and 220°C, the surface coverage of Mg can be estimated qualitative to be 0.05, 0.1, and 0.15, from experimental data of Daudin et al. [3] respectively. With these values of Mg surface coverages, growth rate, G, versus Ga flux, J_{Ga}, plots were obtained using Equation 1.2, 1.3, 2.2, 2.3, and 4.1.and are shown in Figures 2-5 along with the corresponding experimenta1 data [3]. In all three cases, the qualitative agreement between the experimental and theoretical plots is good. Quantitative agreement is only fair due to uncertainty and scatter in the experimental data and in the model parameters.

For the case of residual Mg, the growth rate is linear with J_{Ga} in the Ga-limited regime similar to the C_{Mg}=0 case, except that in this case, due to faster incorporation of Ga through Ga-Mg exchange as described in 2.1, the growth rate is faster. In the low N-limited regime described in 2.2, the growth rate decreases with J_{Ga} given by Equations 2.2 and 2.3. The reason for this observed behavior is as follows. As the Ga coverage, C_{Ga}, becomes more than the N coverage, C_N, there is excess available Ga. Presence of Mg makes the Ga coalesce on the Mg sites, which results in stronger bonding between Ga-Ga resulting in less Ga-Mg exchange. This will result in a decrease in Ga incorporation with the decrease directly proportional to the excess Ga. At a certain J_{Ga}, the excess Ga is exactly equal to the coverage of Mg at which point the growth rate reaches a minimum, which is below the saturated growth rate of the C_{Mg}=0 case. When the excess Ga exceeds the coverage of Mg, the Mg escapes the cluster leaving a ball of Ga and any more excess Ga partly exchanges with Mg or evaporates or agglomerates with the Ga droplet. Thus, the growth rate increases with further increase in J_{Ga} and saturates at a fixed value dictated by the maximum Mg-Ga exchange rate.

In this model, the growth rate dependence on substrate temperature, surface reconstructions, or the growth surface polarity, are not considered. If detailed experimental data for various conditions are available, then a similar model can be adopted and time constants can be obtained by fitting the experimental data to theoretical data. Using the temperature dependence of time constants, activation energies for the various surface processes can be obtained.

4 Conclusion

A rate equation model is developed to investigate the plasma assisted MBE growth of GaN in the presence of fractional monolayer of Mg. Four distinct cases for the model based on the surface processes were identified – (i) Ga-limited regime (ii) Low N-limited regime (iii) Medium N-limited regime and (iv) High N-limited regime. The results of the model were found to be in good agreement with the experimental results of Daudin et al [2]. It is found that exchange between Ga and Mg produces a faster growth rate. Additionally, it is found that non-monotonic behavior of growth rate with Ga flux results due to the dependence of the exchange mechanism Ga cluster size.

ACKNOWLEDGMENTS

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FIGURES

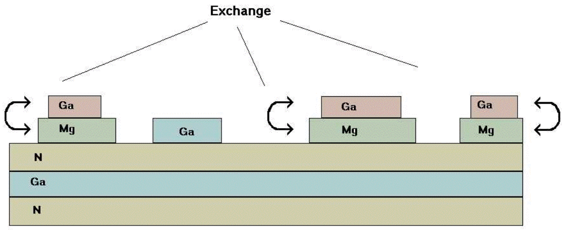

Figure 1a. A schematic picture depicting the incorporation of Ga by Mg and N described in 2.2.

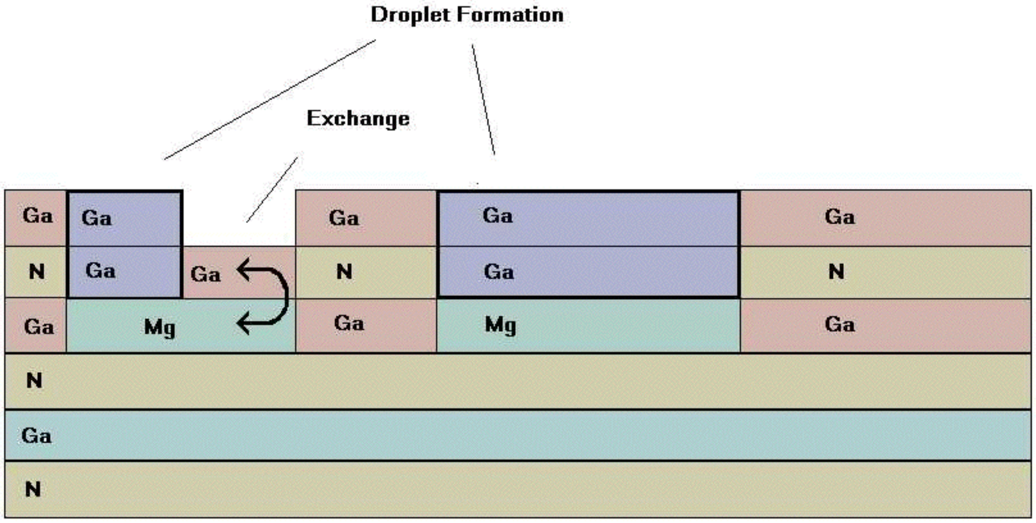

Figure 1b. A schematic picture depicting the formation of Ga droplets due to excess Ga arriving on surface described in section 2.2.

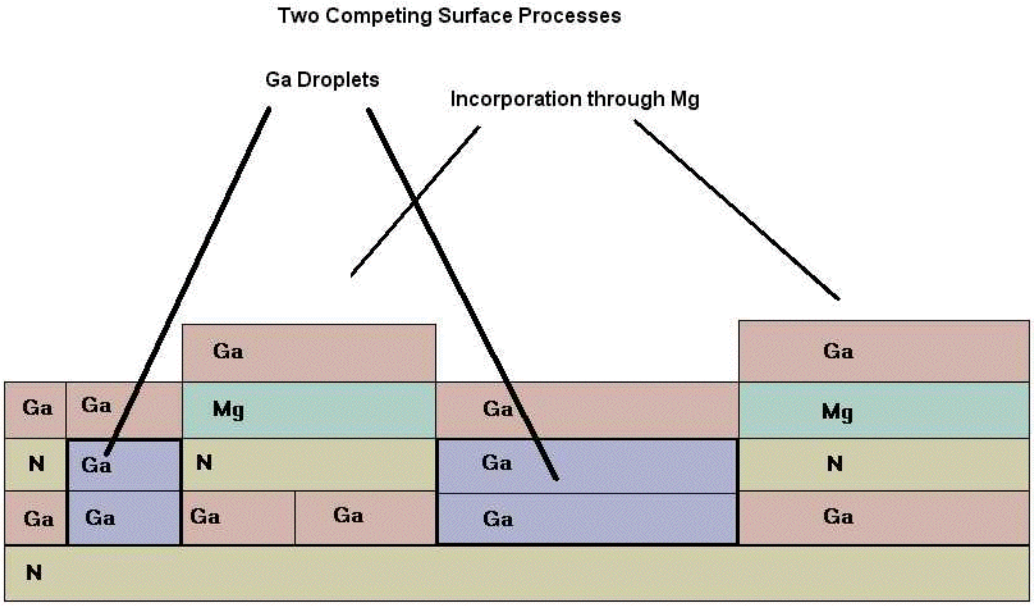

Figure 1c. A schematic picture depicting the segregation of Mg to the surface due to strain forcing Mg to migrate to the surface and two competing surface processes described in 2.2.

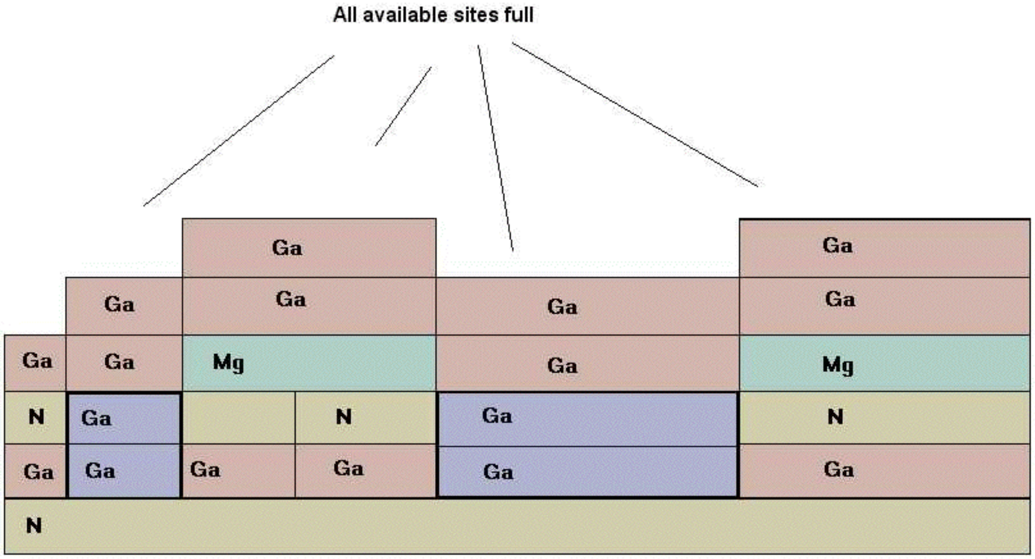

Figure 1d. A schematic picture depicting the surface processes resulting in growth rate saturation described in 2.2.

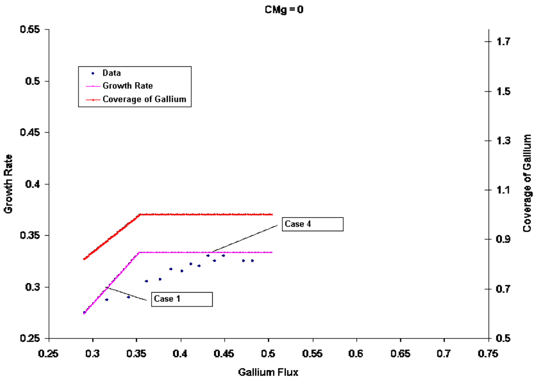

Figure 2. Calculated and experimental growth rate versus Ga flux for the T_{Mg} cell temperature of 0°C corresponding to a C_{Mg} of 0. Coverage of Ga plotted as well.

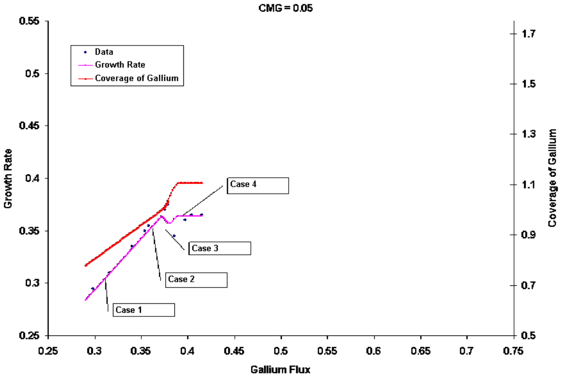

Figure 3. Calculated and experimental growth rate versus Ga flux for residual Mg in the MBE system corresponding to a C_{Mg} of 0.05. Coverage of Ga plotted as well.

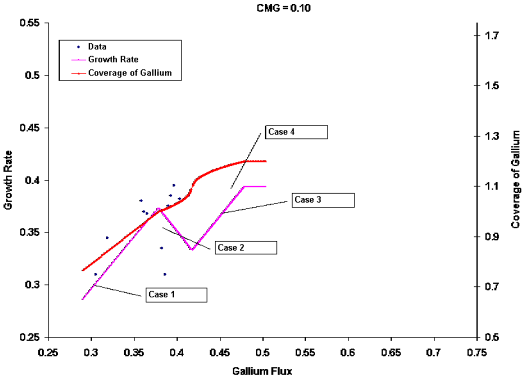

Figure 4. Calculated and experimental growth rate versus Ga flux for the T_{Mg} cell temperature of 212°C corresponding to a C_{Mg} of 0.10. Coverage of Ga plotted as well.

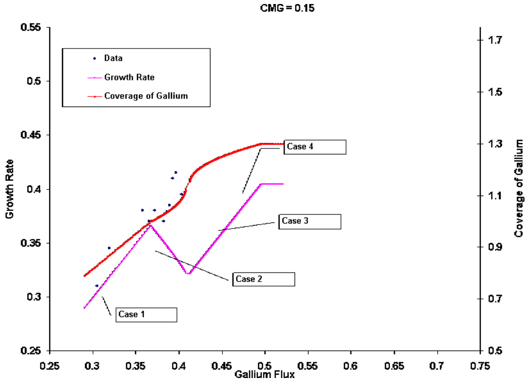

Figure 5. Calculated and experimental growth rate versus Ga flux for the T_{Mg} cell temperature of 220°C corresponding to a C_{Mg} of 0.15. Coverage of Ga plotted as well.

TABLES

Table 1. Dependence of the various τ's on the Mg Surface Coverage.

CMg (ML)	0	0.05	0.1	0.15
τ_1 (s)	3	2.53	2.43	2.25
τ_2 (s)	0	0.35	0.25	0.5
Case 3 multiplier	1	1	0.667	0.541
τ_3 (s)	50	150	200	750
τ_4 (s)	0	15	5	4.75
Case 3 multiplier	1	0.0105	0.025	0.0526