INDIUM SEGGEGATION IN MBE GROWN GAAS/INGAAS/GAAS QUANTUM WELLS

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บทคัดย่อ

การใช้สารกึ่งตัวนำสถานะของแข็งที่ประกอบด้วยธาตุหมู่ 3 และหมู่ 5 สามารถใช้งานได้ดีในเทคโนโลยีการสร้างอุปกรณ์คลื่นไมโครเวฟความเร็วสูงและอุปกรณ์อิเล็คโทรนิกส์ทางแสง ที่ผ่านมามีความพยายามที่จะตรวจวัดการแยกตัวของอินเดียมสู่พื้นผิวที่ตำแหน่งรอยต่อระหว่าง InGaAs/GaAs เพื่อเป็นการปรับปรุงคุณภาพที่รอยต่อดังกล่าว ซึ่งในการศึกษาที่ผ่านมานั้นยังไม่มีวิธีการใดที่เป็นวิธีการวัดการแยกตัวของอินเดียมโดยตรง อีกทั้งเมื่อมีการตีความที่ผิดของรูปแบบการกระจายตัวของปริมาณอินเดียมในระดับชั้นผลึกทำให้เกิดการผิดพลาดในการจำลองสมการทางคณิตศาสตร์เพื่ออธิบายการแยกตัวของอินเดียมบนพื้นผิวผลึก การศึกษาในงานวิจัยนี้ทำการปลูกชั้นผลึกด้วยเครื่องปลูกผลึกด้วยลำโมเลกุล (Molecular Beam Epitaxy) และ เตรียมตัวอย่างด้วยเทคนิคพิเศษเพื่อแปลงส่วนประกอบทางเคมีของชั้นผลึกตามความลึกไปยังพื้นผิวตามระยะแนวราบ และจากการตรวจวัดปริมาณอินเดียมโดยเครื่องไทม์ออฟไฟลท์แมสสเปกโทรเมตรีไอออนทุติยภูมิ พบว่าปริมาณอินเดียมแยกตัวที่วัดได้ในแต่ละตำแหน่งความลึกของชั้นผลึกนั้นขึ้นอยู่กับพารามิเตอร์ในระหว่างการปลูกผลึกได้แก่ อุณหภูมิ สัดส่วนระหว่างปริมาณฟลักซ์ของ As_4 ต่อปริมาณฟลักซ์ของธาตุหมู่ 3 และ อัตราการปลูกผลึกซึ่งขึ้นอยู่กับปริมาณฟลักซ์ของธาตุหมู่ 3 จากการสร้างแบบจำลองเพื่ออธิบายกลศาสตร์การปลูกผลึกด้วยสมการอัตราที่พิจารณาถึงพารามิเตอร์ในระหว่างการปลูกคืออุณหภูมิ สัดส่วนระหว่างปริมาณฟลักซ์ของ As_4 ต่อ ปริมาณฟลักซ์ของธาตุหมู่ 3 และ อัตราการปลูกผลึกโดยพิจารณากับผลที่ได้จากการทดลองและการตั้งสมมุติฐานที่โมเลกุล As_4 ขัดขวางการก่อตัวของธาตุหมู่ 3 เข้าสู่โครงสร้างผลึก พบว่าแบบจำลองนี้สามารถอธิบายปฏิกิริยาระหว่างธาตุหมู่ 3 และ ธาตุหมู่ 5 บนพื้นผิวผลึก

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ที่ปกคลุมด้วยแกลเลียมและพื้นผิวผลึกที่ปกคลุมด้วยอาร์เซนิกในกระบวนการปลูกด้วยลำโมเลกุลได้เป็นอย่างดี

คำสำคัญ: เครื่องปลูกผลึกด้วยลำโมเลกุล, สารกึ่งตัวนำชนิดธาตุหมู่ 3 และธาตุหมู่ 5, การแยกตัวของอินเดียม, เครื่องไทม์ออฟไฟลท์-แมสสเปกโทรเมตรีไอออนทุติยภูมิ

Abstract

Solid state III-V semiconductor device technologies are well established for high speed microwave and optoelectronic devices. Many approaches have been taken to detect indium surface segregation at InGaAs/GaAs interfaces with the purpose of improving interface abruptness. Such studies are not straight-forward and the experimental approaches of many of them misinterpreted indium profiles at the monolayer scale, producing unlikely surface segregation models. The present study employed molecular beam epitaxy (MBE) for layer growth and a novel sample preparation technique was devised which translated vertical chemical depth profiles into horizontal profiles. The use of Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) then allowed vertical indium segregation to be observed and measured. Measured indium segregation profiles are found to depend on the primary growth conditions, substrate temperature, the As_4 to group III flux ratio and the group III growth rate. A rate equation model was developed that incorporates the primary growth parameters, As_4 flux rate, group III growth rate and substrate temperature, to model the growth process kinetically. This fits the experimental data, but only if As_4 molecules are assumed to play a site-blocking role that inhibits the chemical incorporation of the group III elements and indium. This model successfully explains the interaction of the group III and V species on gallium and arsenic terminated surfaces in the MBE growth process.

Keywords: MBE, III-V semiconductors, InGaAs/GaAs, Indium segregation, ToF-SIMS

Introduction

Indium segregation studies performed over the last 25 years mainly involved growing InGaAs on GaAs (100) substrates by MBE. Moison et al. (1989) studied the surface segregation of group III atoms in InAs, AlAs and ternary alloy heterostructures such as $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As$ (x=0.2-0.7) and found that the segregation energies of indium and gallium were in the range of 0.1-0.2 eV and that the segregation tendency followed the trend In > Ga > Al with negligible aluminium segregation. Similar studies by Gérard et al. (1993), Gérard et al. (1995), Nagle et al. (1993), Zheng et al. (1994), Bosacchi et al. (1995), Yamaguchi et al. (1997), Martini et al. (2003) and Mishra et al. (2006), using a variety of physical techniques, produced results in broad agreement with these earliest studies. Since the surface segregation of indium is more obvious than that of gallium and aluminium, Muraki et al. (1992) measured indium segregation lengths in $In_{0.126}Ga_{0.874}As$ MQW structures grown on GaAs (100) substrates and proposed a simple model.

Most previous indium surface segregation studies have employed two main methods. They were (1) to compare indium compositions averaged over a layer of finite thickness with the indium composition in the surface and (2) to measure indium profiles at the bilayer scale. The latter is generally a more useful approach because the indium profiles can suggest the nature of the growth mechanism and the dependence of the indium segregation process on the growth conditions. Such indium profile studies require small sampling depths to minimize averaging effects which may be of the order of segregation lengths and can suggest that segregation is occurring even when it is not. It is therefore important that sampling depths associated with a technique should be measured experimentally.

The model of Muraki et al. is a phenomenological model which lacks physical detail and therefore has no predictive capacity and offers no insights into how the segregation process might be inhibited or prevented. This is in contrast to the model developed here, which has a physical basis and accounts for the dependency of the segregation process on the growth conditions such as As_4 flux rate, group III flux rate and substrate temperature.

The novel sample preparation approach, sample characterization by High Resolution X-ray Diffraction and indium surface segregation measurements by static Time of Flight Secondary Ion Mass Spectrometry which were used here were developed to obtain Indium segregation profiles and have been reported previously (A. Loykaew et al. 2013). This paper proposes a new design of sample structure to provide indium segregation lengths as a function of a variety of growth conditions, presents a kinetic rate equation model todescribe InGaAs segregation and describes a means of extracting Indium segregation lengths from experimental profiles for both rising and decaying indium edges.

Material and Method

A typical structure which was grown is shown in Fig. 1.

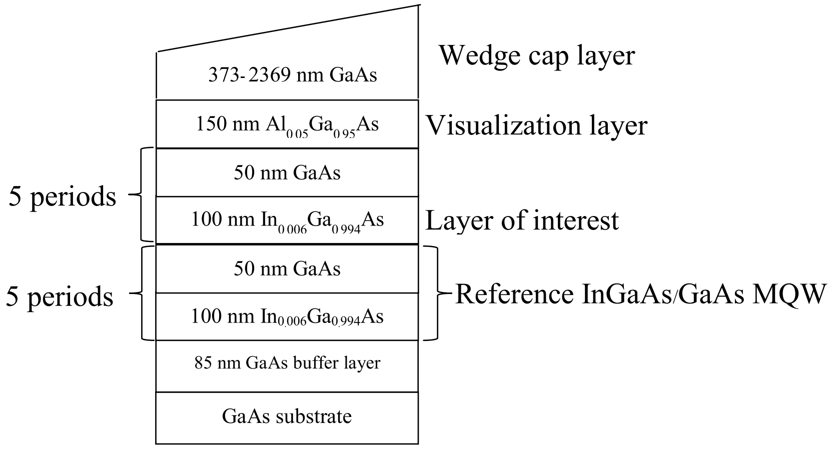

Fig. 1 Sample structure containing a reference InGaAs/GaAs MQW, five InGaAs layers of interest, a 150 nm AlGaAs visualisation layer and the GaAs wedge shaped cap layer.

InGaAs layers were grown with a range of combinations of group III growth rates, As_4 flux rates and substrate growth temperatures and these combinations are shown in table 1. The As_4 flux rates are specified by the multiplication factors which related fluxes to the minimum (optimum under normal circumstances) flux rate employed.

Table 1 The group III growth rates, As_4 flux multiplication factors and substrate growth temperatures used for the growth of the $In_{0.006}Ga_{0.994}As$ layers of interest.

Indium Fraction x	Group III Growth Rates $(\mu m/h)$	As_4 Flux Multiplication Factors	Substrate Temperatures (°C)
0.006	0.20, 0.40, 0.6, 0.8 and 1.00	1, 2, 3, 4 and 5	440, 465, 490, 515 and 540

Table 1 lists the five multiple InGaAs layer samples that were subsequently grown and the conditions under which the InGaAs layers were grown in each of these five samples. The 5th sample which involved growth interruptions was not analysed in the present study. The rise and decay lengths of indium in the wells were measured across the transitions from GaAs to InGaAs and InGaAs to GaAs for the five layers using a ToF-SIMS instrument operating in static mode with a Bi+ primary ion total dose of less than 10^{13} ion.cm^{-2} per pulse with typical pulse lengths of less than a few nanoseconds. Measurements were made by running across an 8 mm x 18 mm etched surface where the etched wedge profile cut through the multi quantum wells structure.

A Kinetic Rate Equations Describing InGaAs Growth by MBE Including Segregation

As_4 processes – on an arsenic terminated surface

The equations which will be presented first relate to As_4 processes occurring on an arsenic terminated surface. Since the only process open to As_4 molecules arriving at a rate J_{As_4} is to thermally desorb with a temperature dependent time constant τ^{V}_{des,As_4} a rate equation describing the physisorbed As_4 population $\vartheta^{V}_{As_4}$ at steady-state is:

$$\frac{d\vartheta^{V}_{As_4}}{dt} = J_{As_4} - \frac{\vartheta^{V}_{As_4}}{\tau^{V}_{des,As_4}} = 0 \qquad (1)$$

As_4 processes – on a group III terminated surface

On the group III surface the dominant As_4 process is the pairwise reaction and a rate equation to describe the physisorbed As_4 population $\vartheta^{III}_{As_4}$ is:

$$\frac{d\vartheta^{III}_{As_4}}{dt} = J_{As_4} - 2\sigma_1 D_{As_4}\left(\vartheta^{III}_{As_4}\right)^2 - \frac{\vartheta^{III}_{As_4}}{\tau^{III}_{des,As_4}} \qquad (2)$$

where consecutive terms on the RHS describe the arrival rate J_{As_4} of As_4 from the vacuum, the rate at which two As_4 molecules meet and participate in the pairwise reaction and the thermal desorption of As_4 molecules from the group III terminated surface. To explain some of the terms, σ_1 is a capture number, D_{As_4} is the diffusion constant of an As_4 molecule in the physisorbed state on a group III surface and τ^{III}_{des,As_4} is a time constant associated with the thermal desorption of an As_4 molecule from a group III surface. It is assumed that the two As_2 molecules produced by the pair-wise reaction immediately chemisorb and the time constant for As_4 desorption is assumed different on a group III surface than on an arsenic terminated surface. The time constant is large enough that the desorption rate is negligible.

As_4 sticking coefficient

As_4 sticking coefficients will depend on the rate at which As_4 desorbs from arsenic terminated surfaces and the rate of the pairwise reaction on group III terminated surfaces. The net incorporation rate of arsenic can be found by summing the incorporation rate due to the pairwise reaction on group III terminated surfaces and the loss due to segregation and subsequent thermal desorption of As_2 molecules from arsenic terminated surfaces. If the fraction of the surface that is group III terminated is designated as θ_{III} then the net incorporation rate can be found by scaling the incorporation or loss processes according to the group III or arsenic surface fractions. The net rate of incorporation I_{As} of arsenic across a surface of mixed terminations is then given by:

$$I_{As} = 4\sigma_1 D_{As_4}\left(\vartheta_{As_4}^{III}\right)^2 \theta_{III} - \frac{2(1-\theta_{III})N_o}{\tau_{seg,As_2}} \qquad (3)$$

Gallium and indium processes

An understanding of the nature of the arsenic terminated surface is required to appreciate the group III kinetics which are relevant to the indium segregation process during growth. For this surface it is assumed that arriving gallium atoms chemisorb with a short time constant $\tau_{Ga,chem}$, the physisorbed gallium population ϑ_{Ga}^{V} on an arsenic terminated surface is therefore:

$$\frac{d\vartheta_{Ga}^{V}}{dt} = J_{Ga} - \frac{\vartheta_{Ga}^{V}(1-F_{As_4})}{\tau_{chem,Ga}} \qquad (4)$$

where J_{Ga} is the gallium flux arrival rate and the second term describes the rate of chemisorption of gallium atoms with a time constant $\tau_{chem,Ga}$. F_{As_4} is a physisorbed As_4 blocking factor expressed as the fraction of potential group III bonding sites that are covered by physisorbed As_4 molecules. This factor can be written as:

$$\vartheta_{In}(0) = \frac{J_{In}\tau_{chem,In}}{1-F_{As_4}}\left(1 + \frac{N_0}{(J_{In}+J_{Ga})\tau_{seg,In}}\right) = \frac{k_1}{k_2}\left(1 + \frac{k_3}{k_4}\right) \tag{5}$$

and $$\theta_{In}(0) = \gamma_1 x_0 = \frac{k_1}{k_4}. \tag{6}$$

Rising edge

The rising edge equation can be approximated by:

$$\frac{x(t)}{x_0} \cong \{1 + \gamma e^{-\alpha_2 t}\} \tag{7}$$

where:

$$\gamma = \frac{-\alpha_3}{\sqrt{(k_2+k_3+k_4)^2-4k_2k_4}} \tag{8}$$

The strongest effect in equation (7) comes from the exponential factor $e^{-\alpha_2 t}$ with γ playing a lessor role in achieving a fit between this approximation and the experimentally observed profiles. γ was therefore initially free to be a fitting parameter less than -1 and following analysis of each of the three sets of experimental data which will yield values for all the k parameters in equation (8), an improved value of γ will be obtained and used in an iterative process to see if the values for α_2 can be improved upon.

Falling edge

The slow root α_4 dominates other than during an initial transient due to the fast root and so falling edge equation can be approximated by:

$$\frac{x}{x_0} = \delta e^{-\alpha_4 t} \tag{9}$$

where:

$$\delta = \frac{\alpha_4-\gamma_1}{\alpha_4-\alpha_5}. \tag{10}$$

The pre-exponential δ was found to be restricted to values greater than 1 and as for the rising edge data δ was initially free to be a fitting parameter and following analysis of each of the three sets of experimental data, an improved value of δ will be obtained and used in an iterative process to see if the values obtained for α_4 can be improved upon.

Results and Discussion

Extracting α values from experimental profiles

Figure 2 in which indium mole fraction in $In_{0.006}Ga_{0.994}As$ is plotted against depth in bilayer shows an example of the ToF-SIMS data obtained from one of five QWs in a sample designed to measure the effect of As_4 flux rate on the indium segregation process. The declining indium signal at the far left of the plot is from another QW presented in the same sample and it is clear that indium levels have declined to background levels before commencement of the rising edge of the QW which is featured in the plot. The background indium level had already been normalized to zero and the QW was thick enough that the indium signal had plateaued before measurements were stopped. Equation (7) could be compared with the experimental profile and the parameters γ and α_2 adjusted to obtain a fit which was matched at the upper end to the plateau. The fitting of the exponential to the data was guided by a least-squares criteria applied over the upper 70% of the transition part of the data, corresponding to the red exponential curve shown in figure 2. A similar procedure was used to obtain the slow root exponent factor α_4 from the falling edge data by matching equation (9) to the experimental data by adjusting the parameters δ and α_4 and the bilayer position at which the exponential should commence.

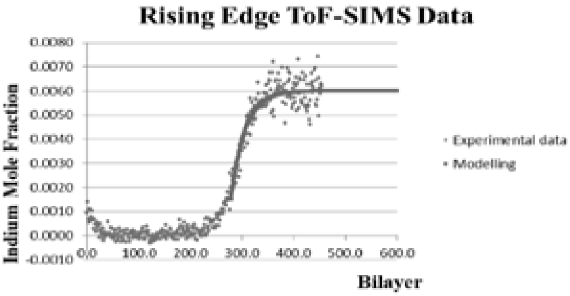

Fig. 2 ToF-SIMS data for a sample which was one of a set measuring the effect of variations in As_4 flux rates on indium segregation lengths.

Multiples of this minimum As_4 flux rate were obtained experimentally using beam equivalent pressure measurements performed to determine the relationship between arsenic furnace temperature and As_4 flux rates. The α_2 and α_4 data is also shown plotted in figure 3 from which, despite considerable scatter in the data, the trends in the two data sets are the same.

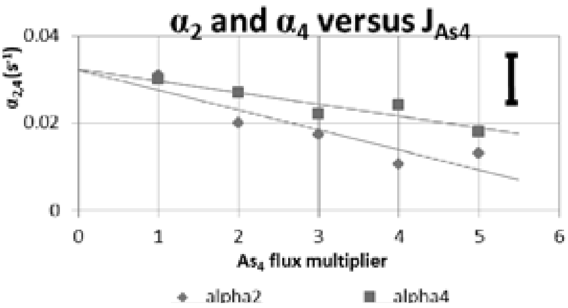

Fig. 3 Plots of α_2 and α_4 versus As_4 flux multiplier. The error bar associated with these measurements is shown in the top right corner of the figure.

A role for physisorbed As_4 in blocking the incorporartion of the group III elements before they even have a chance of being more rapidly locked into the lattice by the faster chemisorption of an overlaying arsenic surface.

Identification of the As_4 site blocking role has successfully explained the observed data and was the only process that was found to give this agreement.

Following a similar procedure as was used to analyse the As_4 flux rate the indium profiles across QWs grown at different substrate growth temperatures and different Gallium flux rates were fitted with exponential functions and the values of α_2 and α_4 obtained are plotted as a function of temperature and Gallium flux in figure 4 and figure 5, respectively.

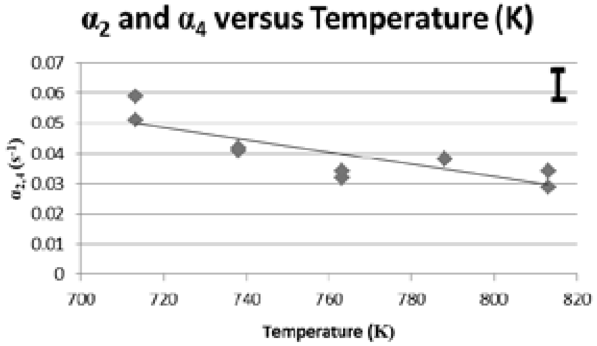

Fig. 4 α_2 and α_4 values plotted as a function of substrate growth temperature (K). The linear trend line is an aid to the eye. The error bar associated with these measurements is shown in the top right corner of the figure.

Most surface processes occurring in MBE growth and similar material systems are thermally activated therefore higher temperature provides more energy to arsenic atom to segregate back to physisorbed state.

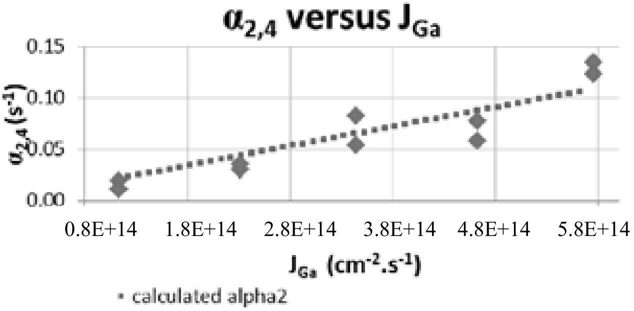

Fig. 5 α_2 and α_4 values plotted as a function of Gallium flux J_{Ga}

The main feature of the experimental group III growth rate data that required explanation was the decrease in indium segregation lengths (increases in α) with increasing growth rates. This behaviour was expected because higher growth rates should result in growth of the next bilayer locking in the indium atoms in the surface, thereby inhibiting the segregation process.

The segregation model was developed to explain the main experimental outcomes of the indium segregation measurements which had been made. These were that (i) an indium segregation process was clearly detected using the experimental approach described in experiment, (ii) indium segregation was more likely at higher substrate temperatures, (iii) indium segregation was suppressed at higher group III growth rates and (iv) indium segregation increased with increasing As_4 to group III flux ratios. The model has similarities with other segregation models although the approach taken to treat group III and group V terminated areas of the surface separately and to formulate different sets of rate equations on each of the surfaces was novel. This approach had the significant benefit that analytical solutions to the rate equations were readily obtained, avoiding the necessity to perform numerical integrations. One of the most important differences between this and other segregation models has been to include an As_4 site-blocking role, which inhibits the chemical incorporation of the group III elements gallium and indium alike on a group V terminated surface.

Conclusions

The use of a kinetic rate equation approach with separate equations for each of the surface terminations was a novel approach and fortunately yielded analytical solutions to all experimental observables of interest. The indium segregation was more likely at higher substrate temperatures and higher As_4 to group III flux ratios due to As_4 site blocking role and thermal activation. On the other hand, indium segregation was suppressed at higher group III growth rates because growth of the next bilayer locks the indium into the crystal structure.

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