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Analysis of the growth modes for gallium arsenide metalorganic vapor-phase epitaxy

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The surface roughness of gallium arsenide (001) films produced by metalorganic vapor-phase epitaxy has been studied as a function of temperature and growth rate by *in situ* scanning tunneling microscopy. Height–height correlation analysis reveals that the root-mean-height difference follows a power-law dependence on lateral separation, i.e., $\Gamma(L)=kL^{a}$, up to a critical distance L_c, after which it remains constant. For layer-by-layer growth, the roughness exponent, α, equals 0.25 ± 0.05, whereas the critical distance increases from 50 to 150 nm as the substrate temperature increases from 825 to 900 K. The roughness exponent jumps to 0.65 ± 0.1 upon transitioning to three-dimensional island growth. By relating the height–height correlation analysis to the Einstein diffusivity relationship, the activation energy for gallium surface diffusion has been estimated: $E_d=1.35\pm 0.1$ eV. © *2000 American Institute of Physics.* [S0021-8979(00)01013-6]

I. INTRODUCTION

The ability to produce atomically sharp compound semiconductor interfaces is of great importance for the development of high-quality heterostructure devices for communications and optical applications. The abruptness of the interface is especially important, where even small deviations at the angstrom level can dramatically affect the electronic properties.[1] An understanding of the factors that influence surface roughening is, therefore, beneficial to improving epitaxial growth procedures. In addition, an objective means of characterizing the surface morphology is important for benchmarking progress.[2]

In previous work, researchers have examined the effects of growth rate and substrate temperature on the morphology of semiconductor thin films grown by molecular-beam epitaxy (MBE).[3–7] The surface roughness has been evaluated by scanning tunneling microscopy (STM) with the aid of height–height correlation functions.[2,4,5] In addition, intensity oscillations observed by reflection high-energy electron diffraction (RHEED) and reflectance difference spectroscopy (RDS) have been analyzed to determine the activation energy for adatom surface diffusion.[6,7] Based on these studies, the accepted energy barrier for gallium adatom diffusion during GaAs MBE is 1.3 eV. Molecular dynamics simulations of the growth process have further substantiated the results obtained from the experimental studies.[8]

On the other hand, fewer studies have been conducted of the growth-mode kinetics of metalorganic vapor-phase epitaxy (MOVPE). Using reflectance difference spectroscopy and grazing-incidence x-ray scattering, several research groups have examined the transition from step flow to island growth.[9,10] Based on this work, an activation energy for gallium adatom diffusion during GaAs MOVPE was estimated to be 2.7 eV, which is unexpectedly large compared to the MBE value. In another study, *ex situ* STM was used to analyze the island growth kinetics.[11] In this case, the diffusion barrier was calculated to be only 0.6 eV. Evidently, more work is needed to establish a consensus on the growth-mode kinetics of the MOVPE process.

In this article, we report on an *in situ* study of the effects of the MOVPE process conditions on the gallium arsenide surface morphology. A scanning tunneling microscope has been interfaced to a MOVPE reactor and utilized to image the film surfaces immediately following growth.[12] Height–height correlation analysis has been employed to determined the dependence of the surface roughness on the substrate temperature and deposition rate. These data have also allowed us to estimate the activation energy for gallium adatom diffusion during GaAs MOVPE.

II. EXPERIMENTAL METHODS

Gallium arsenide films were grown in a horizontal-flow quartz reactor using triisobutylgallium (TIBGa) and tertiarybutylarsine (TBAs) in hydrogen ambient. These alternative sources were used so that epitaxial GaAs films could be deposited at relatively low substrate temperatures, $\leqslant 850$ K. In addition, these sources yield pure films with background carbon doping below 1×10^{16} cm^{-3}, as measured by secondary ion mass spectrometry. The substrates were *n*-type, silicon-doped GaAs(001) wafers ($n=9.0\times 10^{17}$ cm^{-3}) with the surface normal to within 0.1° of the [001] axis. Films were

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deposited at four temperatures, 825, 850, 875, and 900 K, and at three growth rates, 0.25, 0.5, and 1.0 μm/hr. The growth parameters were 0.125–0.5 mTorr TIBGa, 25 mTorr TBAs, 20 Torr H_2, and a linear velocity of 30 m/s (at 298 K and 1 atm). The partial pressures of the precursors were determined in separate experiments in which the compounds were completely decomposed in a quartz tube at 948 K, and the hydrocarbon products measured by mass spectrometry.[13] The mass spectrometer signals were calibrated using hydrocarbon standards.

Prior to initiating growth, the substrates were annealed in 25 mTorr TBAs at 850 K for 10 min to remove the surface oxide. Then, the temperature was adjusted to the desired value and the TIBGa introduced into the reactor for a period of time sufficient to deposit a 0.5-μm-thick GaAs film. Growth was terminated by simultaneously switching off the TIBGa and TBAs. The samples were then cooled to room temperature in flowing hydrogen at 2 K/s. The reactor was evacuated to 2×10^{-7} Torr, and the sample was transferred directly to the ultra-high-vacuum system for surface analysis.

The long-range ordering on the crystal surface was determined by low-energy electron diffraction (LEED). All samples exhibited a weak $c(4\times4)$ reconstruction, commensurate with the high-feed ratio of TBAs to TIBGa (V/III=50–200).[14] Scanning tunneling micrographs of the filled states were taken at a sample bias of -3.6 eV and a tunneling current of 1.0 nA. All the STM images presented below were 2×2 μm^2 in size, and the height data were acquired at a resolution of 256×256 pixels. Images were acquired on different areas of each sample, and no significant difference was observed. The height–height correlation function $G(L)$ was calculated for each individual image, then averaged over four images for each sample.

III. THEORY

The numerical data obtained from the STM measurements are used to calculate the height–height correlation function $G(L)$:

$$G(L)=\langle[h(x_i,y_i)-h(x_j,y_j)]^2\rangle, \tag{1}$$

where $h(x_i,y_i)$ and $h(x_j,y_j)$ are the surface heights at locations i and j separated by a lateral distance, L.[15] The notation $\langle\cdots\rangle$ denotes an ensemble average over all possible pairs of surface points. The results obtained herein will be presented in terms of the root-mean-height difference $\Gamma(L)=\sqrt{G(L)}$.[16]

The root-mean-height difference $\Gamma(L)$ measures the fluctuation of the surface height at a given lateral distance. This function should follow a power-law dependence on the distance up to a certain value denoted as the critical length L_c. Beyond this point, there is no further correlation of the height variation with distance. Expressed mathematically,[17]

$$\Gamma(L)=kL^\alpha, \quad \text{for } L\ll L_c, \tag{2}$$

$$\Gamma(L)=\Gamma(\infty), \quad \text{for } L\gg L_c, \tag{3}$$

where α is the roughness exponent, and k is a constant which can be estimated as

$$k\approx\frac{\Gamma(\infty)}{L_c^\alpha}. \tag{4}$$

The roughness exponents are determined by fitting Eq. (2) to the root-mean-height difference obtained from the STM images.

For layer-by-layer growth, the diffusion length d may be defined as the mean distance an adatom travels on the surface before it is incorporated into the lattice.[18] For GaAs MOVPE at high V/III ratios, the island density is determined by the diffusion rates of the gallium adatoms. It may be assumed that the diffusion length of this species is less than the critical length, in which case there exists a value of the correlation height $\Gamma(d)$ equal to Γ_0:[19]

$$\Gamma_0=kd^\alpha, \quad \text{for } 0<\alpha<1. \tag{5}$$

This height is between 2 and 10 atomic layers of the crystal. Solving for d in Eq. (5) yields[20]

$$d=L_c\left[\frac{\Gamma_0}{\Gamma(\infty)}\right]^{1/\alpha}. \tag{6}$$

Assuming no anisotropy in surface migration rates, the Einstein relation $d^2=2D\tau_D$ may be used to evaluate the $\Gamma(L)$ data. The Ga diffusivity may be described by an Arrhenius relationship, with the diffusion length described by

$$d=\sqrt{2D_0\tau_D}\exp\left(\frac{-E_d}{2k_BT}\right), \tag{7}$$

where D_0 is the attempt rate, τ_D is the residence time of gallium adatoms on the surface, E_d is the activation energy for surface diffusion, k_B is Boltzmann's constant, and T is the temperature. Combining Eqs. (6) and (7) yields

$$L_c\left[\frac{\Gamma_0}{\Gamma(\infty)}\right]^{1/\alpha}=\sqrt{2D_0\tau_D}\exp\left(\frac{-E_d}{2k_BT}\right). \tag{8}$$

The activation energy for gallium surface diffusion can be determined from the slope of a plot of $\log[L_c/\Gamma(\infty)^{1/\alpha}]$ versus inverse temperature. This analysis assumes that the pre-exponential factor D_0 is not a strong function of temperature.

Equation (8) is valid provided that the MOVPE process is at steady state, i.e., the temperature and the partial pressure of the gallium source is constant throughout the nucleation and growth of the GaAs film. In a separate experiment, we found that it takes less than 5 s for the TIBGa precursor to reach a steady concentration in the reactor. On the other hand, island nucleation occurs over a period of 90 s after the onset of growth. Hence, the assumption of steady-state growth conditions is valid.

IV. RESULTS

Shown in Fig. 1 are STM images of the GaAs surface following deposition at temperatures between 825 and 900 K. In all cases, the growth rate equals 0.5 μm/h. An examination of the micrographs reveals that a transition occurs from three-dimensional to layer-by-layer growth upon increasing the temperature from 825 to 850 K. At 825 K, the surface is comprised of large mounds ranging from 0.1 to 0.5

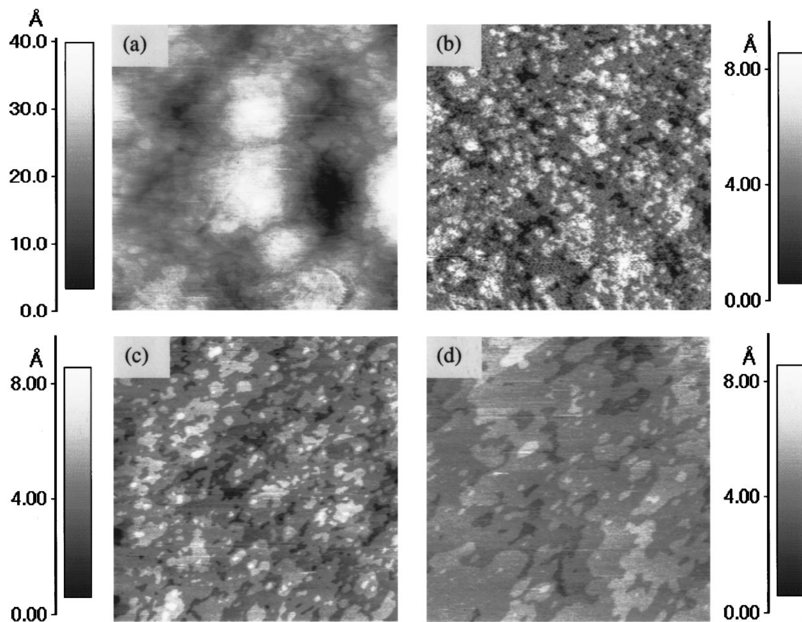

FIG. 1. Scanning tunneling micrographs of the GaAs(001) surface after MOVPE growth at 0.5 μm/h and (a) 825, (b) 850, (c) 875, and (d) 900 K. The images are 2×2 μm^2.

μm in diameter and between 30 and 40 atomic layers in height (40–55 Å). By contrast, the surface roughness is constant above 850 K, and encompasses only 8–10 atomic layers. As the temperature increases from 850 to 900 K, the density of islands decreases, in addition, the islands become elongated in the [110] direction.[11]

Figure 2 shows a series of STM micrographs for GaAs films deposited at different growth rates, but at a fixed temperature of 850 K. The growth rate was proportional to the partial pressure of triisobutylgallium in the MOVPE reactor (i.e., the feed rate of TIBGa). Here as well, the film undergoes a transition from three-dimensional to layer-by-layer growth. This transition occurs when the deposition rate decreases from 1.0 to 0.5 μm/h. These results show that the surface morphology of the films is affected the same way by decreasing the gallium flux as by increasing the substrate temperature.

Presented in Fig. 3 is a log–log plot of the root-mean-height difference as a function of the lateral separation on the surface, for GaAs films grown at different temperatures. The root-mean-height difference rises with the spatial separation up to a certain point and then levels off. The solid lines in Fig. 3 are the best fit of the power-law equation [Eq. (2)] to the data. The slope of the line yields the roughness exponent α, and the knee, where the data deviate from the line, corresponds to the critical length L_c. For three-dimensional growth at 825 K, the roughness exponent equals 0.5, whereas for layer-by-layer growth at 850–900 K, the roughness exponent is substantially smaller, ranging from 0.2 to 0.3.

Further examination of Fig. 3 reveals that the critical length increases with temperature for films following a two-dimensional (2D) growth mode: $L_c = 60$ nm at 850 K, 75 nm at 875 K, and 95 nm at 900 K. These data indicate that for small separations below the critical length, the surface roughness declines as one increases the growth temperature. On the other hand, for large separations above L_c, the surfaces are all equally rough.

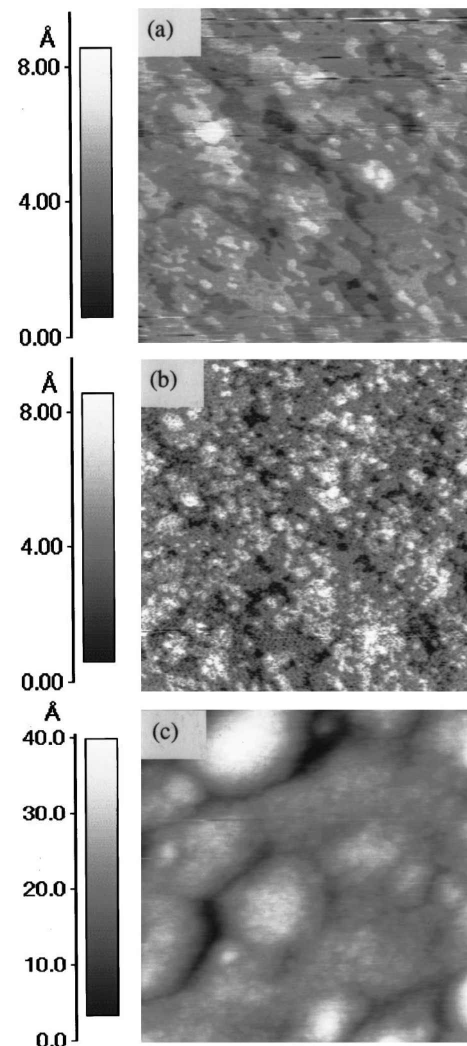

FIG. 2. Scanning tunneling micrographs of the GaAs(001) surface after MOVPE growth at 850 K and a growth rate of (a) 0.25, (b) 0.5, and (c) 1.0 μm/h. The images are 2×2 μm^2.

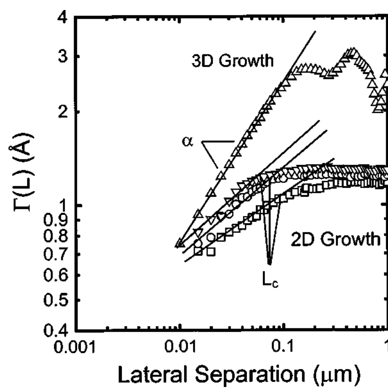

FIG. 3. A log–log plot of the root-mean-height difference with lateral separation. The films were deposited at 0.5 μm/h at (△) 825, (▽) 850, (○) 875, and (□) 900 K.

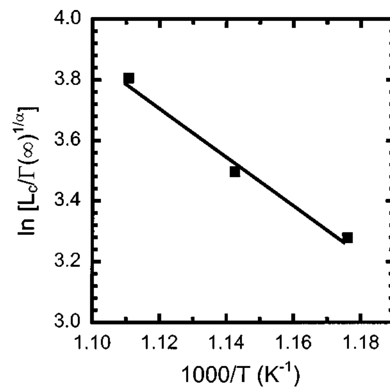

FIG. 5. A semilog plot of the left-hand side of Eq. (8) ($\ln[L_c/\Gamma(\infty)^{1/\alpha}]$) with inverse temperature.

Presented in Fig. 4 is a log–log plot of the root-mean-height difference as a function of the lateral separation, for GaAs films deposited at different rates. The roughness exponent is 0.7 for three-dimensional (3D) growth at 1.0 μm/h, whereas it is 0.3 for layer-by-layer growth at less than 0.5 μm/h. The 3D growth mode generates a rougher surface, which is evidenced by a higher roughness exponent, and a larger value for the root-mean-height difference at the saturation point in the curve. Note that the value of the roughness exponent for 2D growth averages 0.3, irrespective of the temperature and the deposition rate.

From Eq. (8), a plot of the log of $L_c/\Gamma(\infty)^{1/\alpha}$ versus inverse temperature should yield a straight line with the slope equal to $-E_d/2k_B$. In Fig. 5, this plot is presented for the films deposited under the layer-by-layer growth mode. The activation energy obtained therefrom is 1.35±0.1 eV.

V. DISCUSSION

The roughness exponents reported herein are within the range expected for a kinetic roughening process, $(0<\alpha<1)$, and the values are consistent with previous work.[2,4] Lengel *et al.*[2] studied the surface morphology of MBE-grown GaAs(001) using STM. The deposition mode was controlled by adjusting the ratio of the arsenic and gallium fluxes. These authors determined an α of 0.4–0.6 for three-dimensional island growth and 0.2–0.3 for layer-by-layer growth, in good agreement with our study. However, according to dynamic scaling theory, the roughness exponents for these two deposition modes should be 0.67 and 1.0, respectively.[2,21–23] Evidently, this theory is inadequate for describing the vapor-phase epitaxy of compound semiconductors.

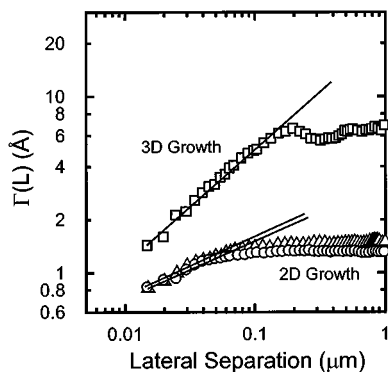

FIG. 4. A log–log plot of the root-mean-height difference with lateral separation. The films were deposited at 850 K at (□) 0.25, (△) 0.5, (○) 1.0 μm/h.

The activation energy for gallium adatom diffusion on GaAs(001) surfaces under MBE conditions has been reported previously.[6–8] Neave *et al.*[6] used RHEED intensity oscillations to study the transition from step-flow to two-dimensional island growth. They assumed that the diffusion length was equal to the terrace width on their vicinal GaAs substrates, and they extracted a surface diffusion barrier of 1.3 eV from the data. Heyn and Harsdorff[8] made similar RHEED intensity measurements during MBE, and obtained an activation energy of 1.4 eV.

In this study, we obtain an activation energy of 1.35 eV for gallium arsenide MOVPE, in good agreement with the MBE work. Moreover, the roughness exponents are the same in both studies. This suggests that the diffusing species controlling the epitaxial growth of the semiconductor film is the same in the MOVPE and MBE processes, i.e., it is the Ga adatoms. One might expect that the alkyl groups present in the former case would influence the surface diffusivity of gallium. However, the butyl groups from TIBGa and TBAs are unlikely to be adsorbed on the surface during growth at 825–900 K. Cui, Ozeki, and Ohashi[24] have shown that these alkyl species rapidly desorb from GaAs(001) above 575 K.

Kisker *et al.*[10] employed *in situ* grazing-incidence x-ray diffraction to follow the transition from step-flow to island growth in their study of the MOVPE process. Based on an analysis of the results, they obtained an activation energy for Ga adatom diffusion of 2.7 eV. This value is considerably higher than that obtained in the MBE studies. Ploska *et al.*[9] also obtained a diffusion barrier of 2.7 eV for MOVPE growth using reflectance difference spectroscopy. It should be noted that both of these authors assumed that the diffusion length of the gallium adatoms before incorporation equals the terrace width. The terrace width was calculated from the degree of offset of the surface normal from the [001] direction. Several other research groups have shown that step

bunching occurs on vicinal GaAs(001) surfaces during arsine annealing prior to MOVPE growth.[25,26] The time required to achieve the step-bunched structure is as little as 5 s. Therefore, the actual terrace width may be significantly larger than that calculated from the miscut angle. This error would lead one to overestimate the activation energy for gallium adatom diffusion, and could explain the discrepancy between the values measured by Kisker and Ploska and those obtained in this work and in the MBE studies.

Kasu and Kobayashi[11] determined the surface diffusion coefficient of gallium species $D(T)$, from STM studies of the island densities on flat GaAs(001) films after MOVPE. The activation energy for surface diffusion E_d was determined to be 0.62 eV from the relationship: $D(T) = a^2 \nu \exp(-E_d/k_B T)$. Kasu and co-workers obtained the STM images in a chamber that was separate from the MOVPE reactor. In order to avoid damage of the surfaces, they deposited a thick layer of arsenic on the crystal surfaces immediately following growth. Then, after transfer to the vacuum system, the samples were annealed to desorb the excess arsenic. We have examined the arsenic capping process and have found that it causes the islands on the GaAs surface to coalesce together. As a result, the effect of the MOVPE process conditions on the film morphology is dampened out, i.e., the island densities become less dependent on the growth temperature. This explains why Kasu and Kobayashi[11] obtained an activation energy for gallium diffusion that was too low.

Recently, Salmi *et al.*[27] conducted molecular dynamics simulations of the diffusion of a single gallium atom on the $c(4\times4)$ reconstruction of GaAs(001). They obtained activation energies for Ga surface diffusion of 0.8 and 1.15 eV in the (110) and $(\bar{1}10)$ directions, respectively. Their results are in reasonably good agreement with the energy barrier of 1.35 ± 0.1 eV measured in this study. In summary, our analysis of the height–height correlation data, e.g., Eqs. (1)–(8), appears to be a valid approach for estimating surface diffusion kinetics.[17,19,20] Nevertheless, more studies of III/V MOVPE are required to fully validate the technique.

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