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LETTER TO THE EDITOR

Crystal growth model for molecular beam epitaxy: role of kinks on crystal growth

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Abstract. A simple crystal growth model for molecular beam epitaxy (MBE) is proposed. Based on the common features of various MBE material systems, growth modes are classified as either high-temperature growth or low-temperature growth. The transition temperature between the two growth modes is found to be a characteristic value: half the melting temperature (T_m) of each material. The incorporation of growing atoms on the crystal surface is discussed based on a crystal surface model composed of kinks, ledges, and terraces. At temperatures higher than $\frac{1}{2}T_m$, kinks act as incorporation and decomposition sites for growing atoms, and the shape of the growth front step is simple and smooth. At temperatures lower than $\frac{1}{2}T_m$, kinks act only as pinning sites with a zigzag step.

The purpose of this letter is to provide a simple guideline and criterion for understanding the crystal growth mechanism in molecular beam epitaxy (MBE). In MBE, a single crystalline layer is epitaxially grown on a crystalline substrate surface by depositing vapour atoms (and/or molecules) in an ultrahigh vacuum (UHV): $\sim 10^{-10}$ Torr). Since a UHV provides both a clean environment and well-defined clean surface substrates, and since a UHV excludes external growth conditions, such as heterogeneous nucleation by contamination, it is considered to be a good environment for growth through accurate control. Hence, the basic study on crystal growth mechanisms of vapour phase epitaxy seems to become possible.

We contend that a universal growth rule can be recognized by extracting the common features from several MBE material systems, because ideal growth occurs in MBE under intrinsic growth conditions. Previously, from a macroscopic point of view, we found a common relationship between crystal quality and growth temperature in various MBE material systems. In this letter, from a microscopic point of view, we propose a growth mechanism in MBE, especially a role of kink sites on growth, based on our previous work, [1, 2].

Crystal quality depends on many factors: growth temperature, growth rate, and substrate crystal orientation, and so on. Here, it is inevitable to maintain molecular beam source purity, substrate surface cleanness, and substrate surface flatness. For compound materials, optimization of molecular beam flux intensity ratio is also inevitable for obtaining stoichiometric composition. Among growth conditions, the growth temperature has the most influence on the quality of epitaxial layer under usual growth rate ($0.01\text{--}1\text{ nm s}^{-1}$)

in MBE [1, 2]. Figure 1 shows the growth-temperature dependence of the crystal quality of epitaxial layers for GaAs layers grown on GaAs(001) substrates obtained by Metzger and Calawa [3], and for Si layers grown on Si(001) obtained by us [2], as typical examples. Here, the temperature scales are normalized to each melting temperature (T_m). For Si MBE, crystal quality is judged by the reciprocal of the electron diffraction spot size. After growth, substrates were cooled to room temperature, and a FWHM (full width at half maximum) of the (0, 1) spot on the first Laue zone is measured using *in situ* reflection high energy electron diffraction observation. Diffraction spots become sharper and clearer as the crystal has higher quality, because a high-quality crystal with low defect density has a sharp reciprocal lattice and low lattice distortion [2]. The temperature dependence of $1/\text{FWHM}$ (\equiv crystal quality) changed at $0.52 T_m$. For GaAs MBE in figure 1, Si atoms were doped into GaAs epitaxial layers at various growth temperatures with the same Si doping flux intensity. Crystal quality for GaAs is judged by the mobility of electric carriers measured at 77 K. It is well known that a dominant scattering mechanism of electric carrier at 77 K is by ionized impurities for the case of the high-quality crystal. In contrast, for the case of the low-quality crystal, some doping atoms are neutralized by the compensating crystal defect of GaAs, and they act as scattering centres of electric carriers [3]. In fact, carrier concentration decreases with decreasing growth temperature due to compensating crystal defects with dopant atoms [3]. Low carrier mobility at low growth temperature in figure 1 is due to the presence of compensating crystal defects. That is, the value of mobility at 77 K is a good indicator of crystal quality from low to high quality. Temperature dependence of carrier mobility (\equiv crystal quality) changes at $0.51 T_m$. Thus, it is easily seen that the temperature dependence of crystal quality changes at $\frac{1}{2}T_m$. Thus, it is easily seen that the temperature dependence of crystal quality changes at $\frac{1}{2}T_m$ for both GaAs and Si. The growth modes can therefore be classified into two categories: the growth mode above this 'transition' temperature, or that below.

Table 1. Transition temperatures of various MBE material systems. Transition temperatures were normalized to the melting temperature (T_m) of each material in absolute temperature scale. Si: $T_m = 1685$ K, GaAs: $T_m = 1511$ K, NiSi₂: $T_m = 1266$ K. Citing works were shown in [2].

MBE material system	Transition temperature	Crystal structure	Reconstruction structure	Bond character
Si on Si(001)	$0.52T_m$	diamond	2×1	covalent
Si on Si(111)	$0.52T_m$	diamond	7×7	covalent
GaAs on GaAs(001)	$0.51T_m$	ZnS	2×4 or $c2 \times 8$	ionic + covalent
GaAs on GaAs(111)	$0.51T_m$	ZnS	2×2 or $\sqrt{19} \times \sqrt{19}$	ionic + covalent
NiSi ₂ on Si(111)	$0.53T_m$	CaF ₂	1×1	metallic

Table 1 lists the transition temperature for several materials and substrate orientations. Transition temperatures are about $\frac{1}{2}T_m$ for every material and substrate orientation dependence was not observed. This suggests that a common growth rule exists in MBE.

As another important experimental result, it is well known that two-dimensional epitaxy (layer-by-layer growth) takes place in MBE growth [4–8]. The experimental results are summarized as follows:

- (i) the growth mode in MBE is classified into two categories, and the transition temperature between the growth modes is $\frac{1}{2}T_m$;
- (ii) two-dimensional epitaxy occurs in MBE.

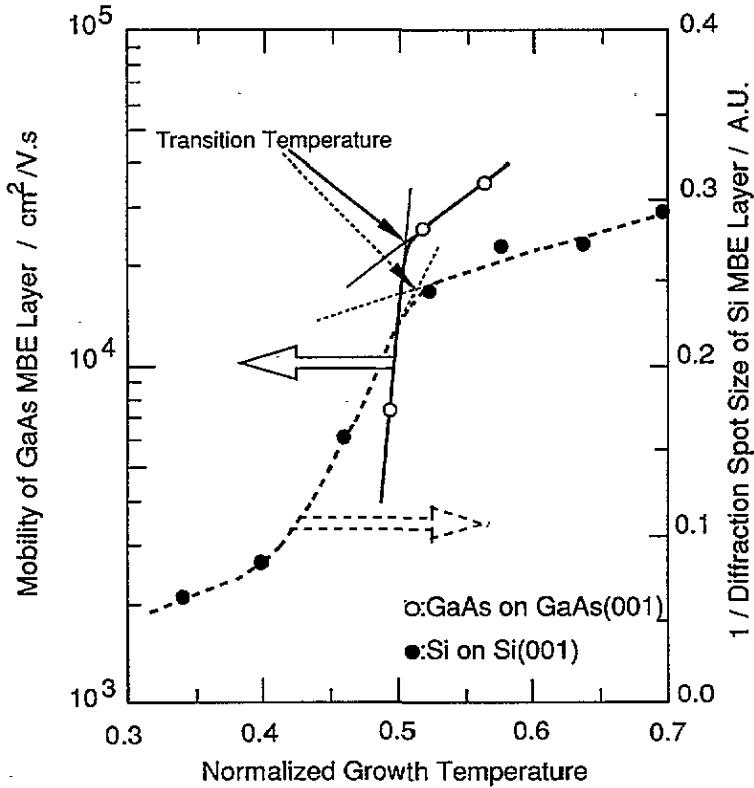


Figure 1. Growth-temperature dependence of crystal quality for GaAs layers grown on GaAs(001) substrates [3] and for Si layers grown on Si(001) substrates [2]. Crystal quality is represented by the mobility of the electric carriers measured at 77 K for GaAs or by the reciprocal width of the electric diffraction spots observed at room temperature for Si. Growth temperatures are normalized to the melting temperature (T_m) of each material (GaAs: $T_m = 1511$ K, Si: $T_m = 1685$ K).

Before discussing a growth rule based on these experimental results, we will consider a surface structure model. Since MBE growth takes place on the crystal surface, a common, simple, and general surface character must be discernible in the various materials, even when their surface orientations or reconstruction structures differ, and even when their bonding characters differ, as experimental results were shown in table 1. The terrace-ledge-kink model proposed by Kossel [9] and Stranski [10] is applicable to various surfaces of different materials as a common feature. This surface structure model is shown in figure 2.

Growing atoms are certainly incorporated at the side of steps, because two-dimensional layer-by-layer growth occurs in MBE. Therefore, among surface atomic sites, only two sites are thought to be incorporated for growing atoms (except for the extremely early stage of two-dimensional nucleation cluster formation on terraces). One is the ledge site and the other is the kink site.

The binding energies of the terrace (E_t), ledge (E_l), and kink (E_k) atoms are roughly in proportion to their coordination numbers, where changes of back-bond energies due to the dangling bond formation are neglected. They increase, in order, as if going up stairs: a zero-order estimation applying the simple cubic atom approximation shows that the ratio of $E_t : E_l : E_k : E_b$ is roughly 1:2:3:6. The reason we normalize to the melting

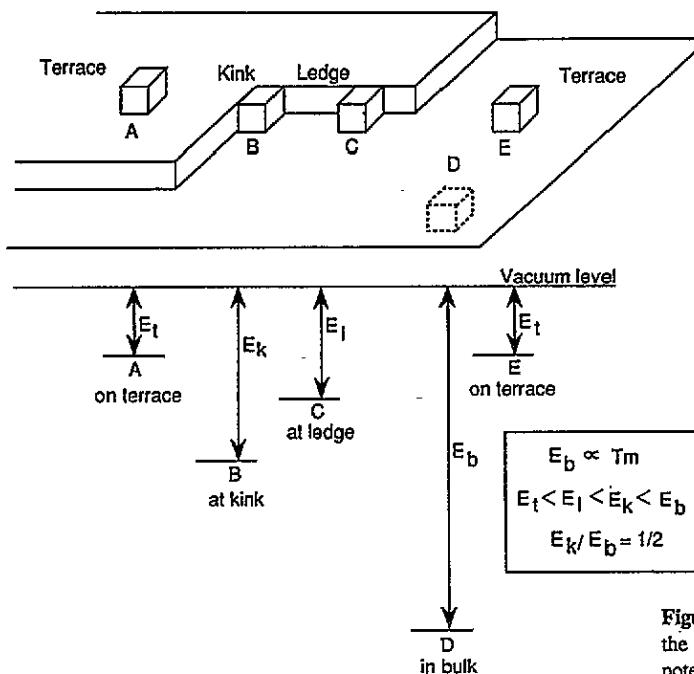


Figure 2. Schematic illustration of the terrace-ledge-kink model and their potential levels.

temperature for each material is because the binding energy of the bulk material (E_b) is linearly related to the melting temperature for each material [2]. Thus, the binding energy for each surface site is normalized to that of bulk for each material. The binding energy of kink-site atoms is half that of bulk-site atoms ($E_k/E_b = \frac{1}{2}$) because kink-site atoms have half the coordination number of bulk atoms, irrespective of the surface orientation [9, 10]. Analogous to the melting of bulk crystal, an atom at a kink site will decompose above $\frac{1}{2}T_m$. Similarly, atoms on terrace and at ledge sites will decompose above $(E_t/E_b)T_m$ and $(E_l/E_b)T_m$, respectively. Both $(E_t/E_b)T_m$ and $(E_l/E_b)T_m$ change, depending on crystal orientation and structure. Thus, the change in growth modes at a characteristic temperature of $\frac{1}{2}T_m$ is thought to be related to kink sites.

Let us try to imagine how growing atoms are incorporated and decomposed at various surface sites with temperatures. Since growing atoms impinge uniformly from the vapour phase onto the crystal surface, they will sink at all surface sites. Roughly speaking, above $(E_t/E_b)T_m$, atoms bound on terraces can move: two-dimensional epitaxy occurs. Above $(E_l/E_b)T_m$, atoms bound at ledge sites can decompose: some recovery phenomena of crystal quality occurs. Above $\frac{1}{2}T_m$, atoms bound at kink sites can decompose: heavy recovery occurs. Indeed, as the experimental results of Si on Si(001) MBE, the critical temperatures are as follows: epitaxial starting temperature changes from 0.18 to $0.29T_m$ depending on grown layer thickness and growth rate [2, 11], generation of crystal defect varies at $0.35T_m$ [11] at a growth rate of 0.1 nm s^{-1} , and crystal quality changes at $\frac{1}{2}T_m$ as shown in figure 1. Since the former two temperatures change depending on many factors, as mentioned above, the following discussion will centre on the role of kinks on crystal growth, which will be distinguishable at $\frac{1}{2}T_m$.

Figure 3 shows a schematic illustration of the MBE growth model. Figure 3(a) shows the ledge growth when growth temperature is lower than $\frac{1}{2}T_m$. If one straight step is assumed

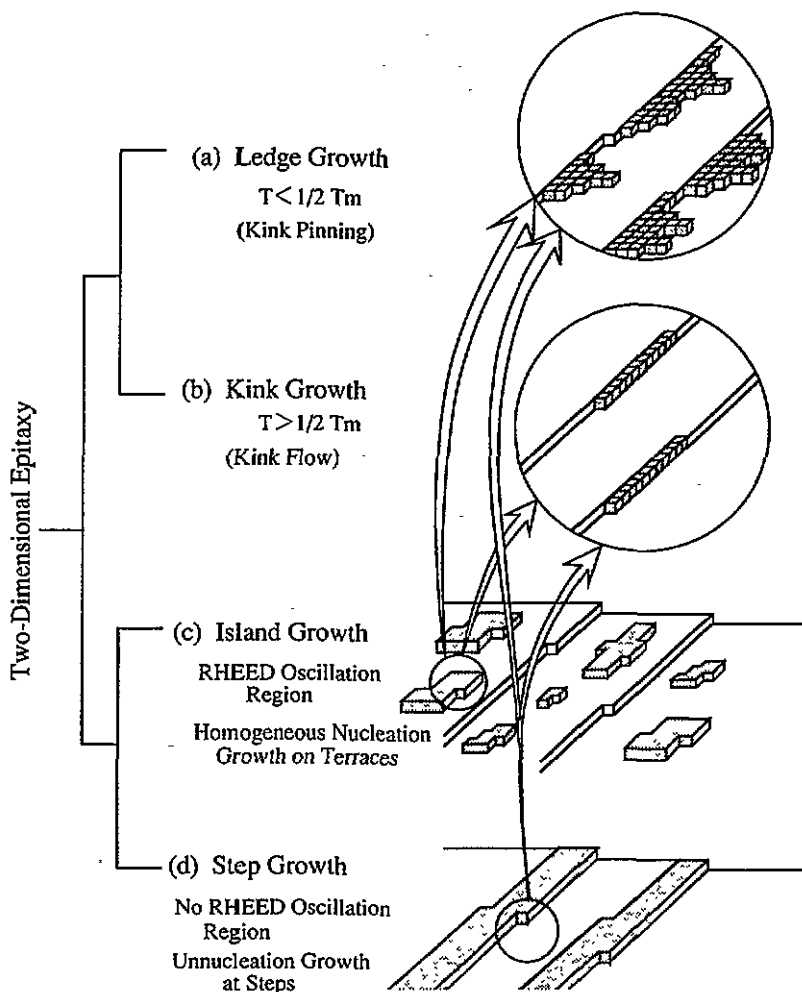


Figure 3. Schematic illustration of the growth model in MBE. Two classifications of two-dimensional epitaxy are presented: One ((a) and (b)) is proposed by us and the other ((c) and (d)) was proposed by Joyce *et al* [5,6]. (a) Growing atoms incorporated at the atomic site of ledges and kinks. Since kinks act as a pinning point at temperatures lower than $\frac{1}{2}T_m$, the growth front becomes zigzag. (b) Growing atoms are incorporated and decomposed at atomic sites of kinks at temperatures higher than $\frac{1}{2}T_m$. The growth front becomes smooth, because kink sites do not act as pinning sites. (c) Two-dimensional nuclei and islands grow at regions on the terraces. Diffraction intensities oscillate synchronously with each atomic layer growth. (d) Growth takes place at the region of steps without nucleation. No oscillation phenomena of diffraction intensities were observed.

as a starting point for the growth, growing atoms will be incorporated at every site along the step. As the growth proceeds, the shape of the growth front will become zigzag, with many kinks and short ledges, because kink sites act as pinning points.

Figure 3(b) shows the kink growth when growth temperature is higher than $\frac{1}{2}T_m$. The shape of the growth front will become straight because kink sites do not act as pinning points, and because a straight step has the minimum energy. Decomposed atoms from kink sites will migrate onto terraces: some of them will vaporize into the vacuum, while

the rest will incorporate again at kink sites. A dynamic incorporation and decomposition process therefore takes place at kink sites. This dynamic process is important for growing high-quality crystal layers. Note that growing atoms are bound only at kink sites, because all of the unvaporized atoms on terraces are surely incorporated at kink sites. The growing atoms at kink sites are bound more strongly, and are thus in a more stable state than atoms at ledge sites. The crystal quality of the epitaxial layer is therefore greatly improved above $\frac{1}{2}T_m$.

To compare our classification in two-dimensional epitaxy with the other, figure 3(c) and (d) is shown: two-dimensional nuclei following islands grow on terraces in (c), and growth takes place at a step region without nucleation in (d). This classification was proposed by Joyce *et al* [5, 6] to explain the oscillation phenomenon of diffraction intensity, which changes synchronously with each atomic layer growth. Note that the edges of the two-dimensional islands in (c) are topologically equivalent to the steps, and that the edges of islands consist of ledges and kinks, exactly like those at the edges of steps. Thus, ledge and kink growth proposed in this work can be applied to both (c) and (d), as shown in figure 3. A fundamental difference in classifications between (a) and (b), and (c) and (d) is whether growth occurs at atomic sites (ledges and kinks) or at regions (steps and terraces). Note again that the growth model by Joyce *et al* (c) and (d) shows only whether nucleation takes place on terraces or unnucleation growth occurs at steps. Another difference is concerned with the transition temperature: the transition temperature between (c) and (d) varies as a function of the growth rate and the terrace width, because it is determined by the adatom mobility on terraces and the terrace width which nucleation growth on terraces or unnucleation growth at steps occurs. On the other hand, the transition temperature between (a) and (b) is constant at $\frac{1}{2}T_m$, because it is related only to the kink site. Thus, the growth mechanism shown in figure 3(a) and (b) is the elemental process for incorporation of growing atoms.

Although it contains some simple and rough estimations, we think our growth criterion provides a unified view of the MBE growth mechanism, and that it can be applied to various surface phenomena, such as surface transition [12] and the surface reaction between gases and crystals.

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