

# A lateral growth mode leading to successive rotation of crystallographic orientation

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**A general theory of heteroepitaxial lateral growth of nanocrystallites via successive nucleation at the concave corner of the nanocrystallite and the substrate was developed. The theory treats the existence of a rotational instability of crystallographic orientation induced by the imbalance of surface/interface energy. From the theory it can be concluded that the crystallographic orientation may rotate continuously, sustained either by consecutive changes of facets on the growth front or by periodic modulation of surface energy of the substrate. Copyright © 2006 John Wiley & Sons, Ltd.**

**KEYWORDS:** lateral growth; nucleation; growth theory

## INTRODUCTION

Thin film growth may start by nucleation on a foreign substrate because the formation of three-dimensional (3D) or two-dimensional (2D) islands on surfaces is often thermodynamically favored over that on uniform films or random adatom distributions under crystal growth conditions.<sup>1</sup> According to the equilibrium theory, heteroepitaxial growth can be categorized into three modes: Frank–van der Merwe (FM), Stranski–Krastanow (SK), and Volmer–Weber (VW), depending on the interfacial energies. These growth modes are often termed as layer-by-layer growth, layer-by-layer plus island growth, and island growth, respectively. Despite the developments in the understanding of thin film growth, little attention has been paid to the dynamic process of horizontal expansion of a crystalline island on a foreign substrate to date. Since the foreign substrate always emerges in the whole lateral expansion process, it may affect the growth dynamics and the final morphologies.<sup>2,3</sup> An interesting example is the small tilting of the crystallographic orientation observed during the lateral overgrowth of GaN from stripes patterned in a SiO<sub>2</sub> mask.<sup>4–6</sup> A theory dealing with this type of phenomena has still not been formulated.

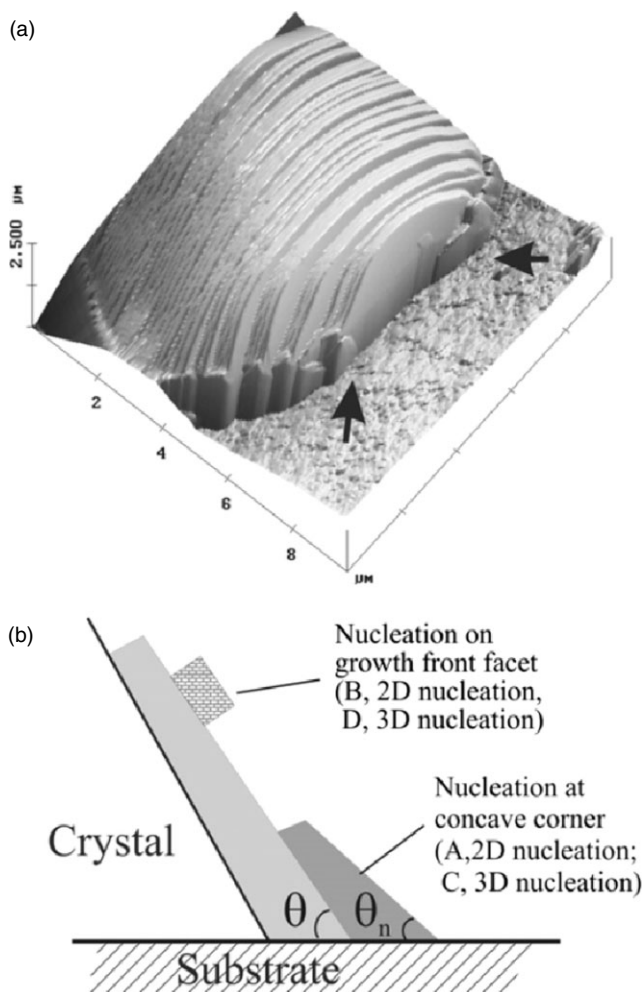
To study the lateral growth process, a series of experiments have been conducted to pinpoint the details of the lateral growth process.<sup>7–9</sup> Crystallization was carried out in a thin layer of agarose gel containing NH<sub>4</sub>Cl or CsCl, sandwiched by two glass plates 100 μm apart. The supersaturation for crystallization was established by evaporating

water through the edges of the glass plates. Although the observed morphologies vary from ramified zigzag branches to straight branches depending on the concentration, the common feature of the crystalline aggregate is the consecutive rotation of crystallographic orientation in lateral growth. The difference in morphology results from the difference in rotation axis and growth direction. The foreign substrate is suggested to play a critical role for the observed phenomena.<sup>7–9</sup> In this paper, we present a brief theory of the consecutive rotation of crystallographic orientation in the nucleation-limited lateral growth of a crystallite on a foreign substrate. More details will be published in a separate paper elsewhere.<sup>10</sup>

## EXPERIMENTAL

A substrate can usually lower the nucleation barrier. Meanwhile, it slows down the kinetics by decreasing the effective kinetic area for receiving growth units. For lateral growth, we found that the crystalline islands develop horizontally slice-by-slice, as shown in Fig. 1(a). In this case, by increasing the growth-driving force, the preferred nucleation processes listed according to their degree of availability are (Fig. 1(b)): 2D nucleation at the corner site (scenario A), 2D nucleation on the growth-front facets (B), 3D nucleation at the corner site (C), 3D nucleation on the growth-front facets (D).<sup>2,3,7</sup> Assuming that the transport and kinetics are fast processes in comparison with the nucleation process, the growth is nucleation-limited and is determined by minimization of the nucleation barrier. In this case, 2D nucleation of a new layer is preferable at the corner site of the precedent layer and the foreign substrate (scenario A in Fig. 1(b)). The asymmetric surface energies of the two substrates at the corner may lead to some unusual phenomena.

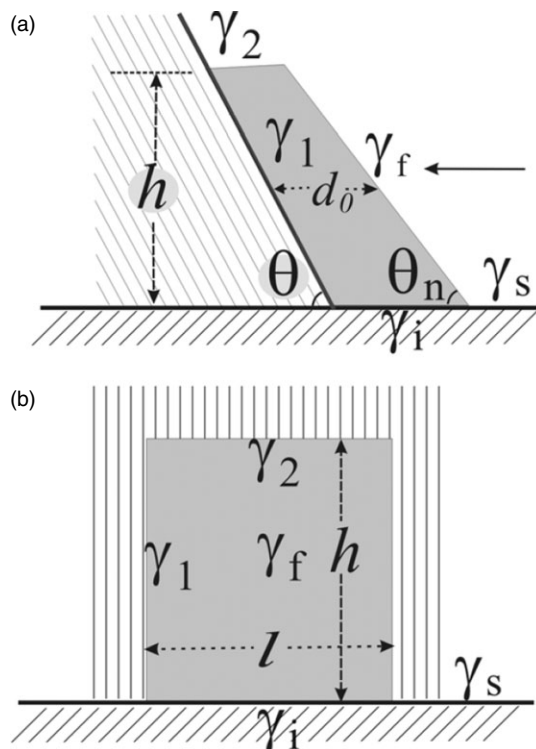
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**Figure 1.** (a) Atomic force microscope (AFM) view of the very front tip of an aggregate branch of NH<sub>4</sub>Cl, from Ref. 7. Nucleation appears at the concave corner of the crystal facet and the glass substrate, which acts as the step source, as indicated by the arrows. The crystal develops forward layer by layer. (b) A schematic illustration of two possible nucleation sites on the growth front at the concave corner site (scenario A and C) and on the growth-front facet (B and D). For each of the sites there are possibilities of 2D nucleation (A and B, with thickness of single atomic layer) or 3D nucleation (C and D, with thickness of multi atomic layer), depending on the growth-driving force.

### MODELLING AND DISCUSSION

Now we apply the nucleation theory to the concave-corner-mediated lateral growth. A schematic diagram is shown in Fig. 2, where the embryo of the nucleus is modeled as a rectangle with height  $h$  and length  $l$ , and the lateral thickness of the embryo at the half height is  $d_0$ . For simplicity, we ignore the structure of the foreign substrate.  $d_0$  is a constant in the case of 2D nucleation at the corner site of the precedent layer and the foreign substrate (scenario A in Fig. 1(b)). Let  $\gamma_f$ ,  $\gamma_s$  and  $\gamma_i$  represent, respectively, the interface energies of nucleus-fluid, substrate-fluid and substrate-nucleus, and  $\theta$  and  $\theta_n$  denote the contact angle of the crystal facet and the nucleus, respectively. In general,  $\theta_n$  is different from  $\theta$ , because it must satisfy different surface/interface energy



**Figure 2.** Schematic of a 2D nucleus on the corner site formed by the growth front and the substrate in lateral growth process: (a) is the side-view plot and (b) is the plot viewed from the growth direction, as shown by the arrow in (a).

relations. This means that the newly nucleated layers (atomic planes) will be slightly rotated with respect to the previously grown atomic layers. The change of surface contact angle  $\theta = \theta_n - \theta$ , represents the degree of crystallographic rotation during lateral layer-by-layer growth. We can write down the total free energy of the 2D nucleus. Minimizing the total free energy with mismatch, which is defined as the crystallographic orientation difference  $\Delta\theta$  between the growth-front facet and the nucleus, we get the mismatch angle  $\Delta\theta$  as a function of the angle  $\theta$  between the facet and the substrate,<sup>10</sup>

$$\Delta\theta = \frac{d_0}{k_\mu h^2} \left[ (\gamma_f \cos \theta + \gamma_i + \gamma_s - \gamma_h/2) - \frac{\Delta\mu}{\gamma_h v_c} \frac{d\gamma_i}{d\theta} d_0 \sin^2 \theta \right] \quad (1)$$

where  $\Delta\mu$  is the difference of chemical potential between crystal phase and fluid phase,  $k_\mu$  is the elastic parameter of the crystal, and  $v_c$  is the atomic volume.  $\gamma_h = \gamma_2 + \gamma_i - \gamma_s$ ,  $\gamma_2$  denoting the surface energies of the side faces of the nucleus, as shown in Fig. 2.

The rotation of the crystallographic orientation induces strain, and hence increases the elastic energy. This disadvantage is compensated by the energy gain in lowering the interface energy between the crystal and the substrate. Although the strain energy is independent of the sign of strain, the interface energy is different for  $\pm\Delta\theta$ . At the very beginning of lateral growth, a 3D nucleus forms on the flat foreign substrate whose initial contact angle is determined by  $\gamma_f \cos \theta + \gamma_i - \gamma_s = 0$ . Thus,  $\Delta\theta$  is generally negative according to Eqn (1), in agreement with experimental observation.<sup>7,8</sup> If the crystal had matched the foreign

substrate completely, i.e.  $\gamma_h = \gamma_2 + \gamma_i - \gamma_s = 0$ , Eqn (1) would give  $\Delta\theta = 0$  for near-equilibrium growth with low supersaturation. In such a scenario, the crystallographic orientation would be naturally preserved. A corresponding case is the laterally expanding stage of a sub-layer during the layer-by-layer epitaxial growth mode.

Equation (1) also indicates that the crystallographic rotation is not a constant but depends on the size of the crystallite, with  $\Delta\theta \propto (1/h^2)$ . It means that the crystallographic rotation can be inhibited by increasing the film thickness, consistent with the observation in lateral overgrowth experiments.<sup>7-9</sup> Physically, this is because the crystallographic rotation in a thick film costs too much strain energy.

Since  $\Delta\theta$  is a function of  $\theta$ , it changes continuously as the lateral growth proceeds via the same slice-by-slice nucleation/growth mechanism and the crystal laterally expands over the foreign substrate. An equilibrium angle  $\theta_{eq}$  could be determined by setting  $\Delta\theta = 0$  as

$$\gamma_f \cos \theta_{eq} + \gamma_i - \gamma_s = \frac{\gamma_h}{2} + \frac{\Delta\mu}{v_c} \frac{d \ln \gamma_h}{d\theta} d_0 \sin^2 \theta_{eq} \quad (2)$$

We note that  $\theta_{eq}$  is different from the wetting angle  $\theta_c$ , which is determined by  $\cos \theta_c = (\gamma_s - \gamma_i)/\gamma_f$ , because firstly, the nucleus is effectively a stressed/strained island where the contact angle becomes size dependent, as shown recently by Liu,<sup>11</sup> and secondly,  $\theta_{eq}$  depends additionally not only on the surface energy but also on the driving force of growth denoted as  $\Delta\mu$ .

The above analysis is based on the assumption that the growth-front face keeps fixed to one low-index facet during the growth process. In this case, the rotation of crystallographic orientation would stop once the surface contact angle of the growth-front facet decreases to the equilibrium value  $\theta_{eq}$ . However, the growth face becomes unstable when the contact angle of the front facet is too small, because a step (new facet) will emerge at the corner. This is equivalent to the Wulff construction of the equilibrium crystal shape: the total free energy of the crystal should be minimized with respect to the proportion of different facets.<sup>12</sup> It is noteworthy that as  $\theta$  decreases, the area of the front-most facet increases. Consequently, there exists a critical angle  $\theta_{cri}$ , below which the original facet ( $S_a$ ) decomposes and a new facet ( $S_b$ ) occurs. After some simple calculations, we can write the equation that determines the value of the critical angle  $\theta_{cri}$ ,

$$\frac{\cos \theta_{cri} + (\gamma_i - \gamma_s)/\gamma_f^a}{\sin \theta_{cri}} = \frac{\gamma_f^b/\gamma_f^a - \cos \alpha}{\sin \alpha} \quad (3)$$

where  $\alpha$  is the angle between facets  $S_a$  and  $S_b$ . Clearly, the scenario discussed in the previous paragraphs can only take place if  $\theta_{eq} < \theta_{cri}$ . After  $S_b$  emerges, it develops and then becomes the dominating atomic plane on the lateral growth front. Similar to what happened to  $S_a$ , there exists for  $S_b$  another equilibrium contact angle,  $\theta'_{eq}$ , and critical angle,  $\theta'_{cri}$ , which defines a critical angle for the emergence of the new facet  $S_b$ . Evidently, if  $\theta'_{eq} < \theta'_{cri}$  is again satisfied, the facet decomposition resumes. This process could repeat infinitely. Practically, however, owing to the surface energy

anisotropy, when the crystal rotates about certain axes, the emerged facets are limited to a few low-index faces. For example, when a fcc crystal rotates about  $\langle 100 \rangle$ , the possible facets on the growth front can only be (001) and (110)/(111). As a result, the crystallographic orientation of the growth front will switch repeatedly between  $S_a$  (001) and  $S_b$  (110)/(111).<sup>7-9</sup>

Except that alternate growth-front faces may cause a never-ending rotation of crystallographic orientation, we predict on the basis of our theory that this phenomenon can be observed when the substrate alternatively changes during the lateral overgrowth process. When the substrate changes, the equilibrium angle  $\theta_{eq}$  changes accordingly. Crystallographic orientation is driven to rotate in order to reach the new  $\theta_{eq}$ . If the surface energy of the substrate is periodically modulated, the rotation may be sustained. We suggest that this is the physical reason of the frequently observed crystallographic tilting during the lateral overgrowth of GaN from stripes patterned in a SiO<sub>2</sub> mask.<sup>4-6</sup>

## CONCLUSIONS

In conclusion, we have developed a general theory of heteroepitaxial lateral growth of nanocrystallites via successive nucleation at the concave corner of the nanocrystallite and the substrate. We have demonstrated the existence of a rotational instability of the crystallographic orientation induced by the imbalance of surface/interface energy. We suggest that the crystallographic orientation can be continuously rotated, which may be sustained either by consecutive changes of facets on the growth front or by periodic modulation of surface energy of the substrate. Quantitatively, by using the parameters of the surface energies and the interface energies, one can get the equilibrium angle and the critical angle, according to Eqn (2) and Eqn (3), respectively. Connected with the crystallographic structure of the growing crystal, it is possible to compare the theoretical results and the experimental observations.

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## REFERENCES

- Zinke-Allmang Martin, Feldman LC, Grabow MH. *Surf. Sci. Rep.* 1992; **16**: 377.
- Hurle DTJ (ed.). *Handbook of Crystal Growth: Thin Films and Epitaxy*. North-Holland: Amsterdam, 1994.
- Lewis B, Anderson JC (eds). *Nucleation and Growth of Thin Films*. Academic Press: London, 1997.
- Fini P, Zhao L, Moran B, Hansen M, Marchand H, Ibbetson JP, DenBaars SP, Mishra UK, Speck JS. *Appl. Phys. Lett.* 1999; **75**: 1706.
- Fini P, Munkholm A, Thompson C, Stephenson GB, Eastman JA, Murty MVR, Auciello O, Zhao L, DenBaars SP, Speck JS. *Appl. Phys. Lett.* 2000; **76**: 3893.
- Dürr AC, Schreiber F, Ritley KA, Kruppa V, Krug J, Dosch H, Struth B. *Phys. Rev. Lett.* 2003; **90**: 16104.

7. Wang M, Li DW, Shu DJ, Bennema P, Mao YW, Pan W, Ming NB. *Phys. Rev. Lett.* 2005; **94**: 125505.
8. Wang M, Liu XY, Strom CS, Bennema P, van Enkevort W, Ming NB. *Phys. Rev. Lett.* 1998; **80**: 3089.
9. Li DW, Wang M, Liu P, Peng RW, Ming NB. *J. Phys. Chem. B* 2003; **107**: 96.
10. Shu DJ, Wang M, Li DW, Liu F, Zhang ZY, Peng RW, Pan W, Ming NB, to be published.
11. Liu F. *Phys. Rev. Lett.* 2002; **89**: 246105.
12. Pimpinelli A, Villain J. *Physics of Crystal Growth*. Cambridge University Press: Cambridge, 1998.