Shape of Heteroepitaxial Island Determined by Asymmetric Detachment

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Square lattice gas models for heteroepitaxial growth of organic semiconductors in relation to the fabrication of thin and deformable microelectronic or optoelectronic devices [1, 2, 3]. To accomplish a high standard in electrical properties, improvement of the film quality is indispensable, and fundamental researches on growth mechanisms of adsorbed organic molecules are undertaken [4, 5]. In an experiment of pentacene (Pn, C$_{22}$H$_{22}$) growth on Si(001) [6], authors concluded that an organic thin-film growth is similar to the epitaxial growth of inorganic materials, such as the formation of fractal ramified islands like diffusion-limited aggregates (DLA) [6, 7].

On the other hand, in an experiment of Pn growth on a hydrogen-terminated Si(111) surface [H-Si(111)] [8], a peculiarity is found. On a flat H-Si(111) surface islands are compact with smooth edges and isotropic, whereas on a vicinal surface islands are dendritic in the step-down orientation while edges in the step-up orientation remain compact: Each island has a strong anisotropy in its shape on a vicinal substrate. Island shape anisotropy, however, is not specific to a vicinal surface. It is observed in the vapor growth of another organic molecule, a behenic acid, even on a flat singular substrate, namely on an oxidized GaAs [8]. In the present paper we analyze some model systems which lead to shape anisotropy theoretically.

In the heteroepitaxial growth of inorganic materials, island shape is mainly controlled by the competition of two processes after an adatom deposition: an adatom diffusion on a terrace surface and an incorporation kinetics at island edges [9, 10, 11, 12]. With a fast incorporation at island edges, diffusion controls the growth and edges undergo a morphological instability to form dendrites. In the extreme case of irreversible solidification such that an adatom once solidified never detaches again from the island edge, then an island takes a ramified irregular shape with many branches [13]. Its structure is similar to the DLA without a characteristic length, and is called a fractal. An island is isotropic or symmetric by reflecting the lattice symmetry.

To provide a compact island shape, edge smoothening processes are necessary, such as an edge diffusion or a detachment from the edge. If the detachment rate is high, adatoms loosely attached to the edge will readily detach and they are hardly incorporated in two-dimensional (2D) islands. Then, the slow incorporation kinetics governs the growth to make islands compact with smooth edges [14, 15, 16]. Islands may be round at high temperatures or polygonal at low temperatures.

In the heteroepitaxial growth of organic molecules, one has to take an additional feature into account, i.e., the size of an adsorbed organic molecule. It can no longer be regarded as a point object as in inorganic cases so far discussed. Both pentacene and behenic acid molecules are flat and elongated in shape. When they are adsorbed on a substrate, molecules can be normal or lateral to the substrate surface [17]. Pentacene molecules are known to grow a wetting film with the molecular long axis normal to the H-Si(111) surface, namely in a standing-up orientation [17]. Behenic acid is also known to be in a stand-up orientation but with a small tilting on a substrate. We assume that this molecular orientation affects the detachment rate of molecules from island edges, and leads to anisotropy in an island shape.

In a previous study [19] we proposed a simple lattice gas model, and studied general aspects of the effect of anisotropic detachment on an island shape. In the next §2 we introduce the model with simulation results of island shapes on a flat substrate. The model is extended in §3 so as to include the effect of steps explicitly for the case of adsorption on a vicinal substrate. The last §4 summarizes the result.

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I. INTRODUCTION

There have been increasing interests in heteroepitaxial growth of organic semiconductors in relation to the fabrication of thin and deformable microelectronic or optoelectronic devices [1, 2, 3]. To accomplish a high standard in electrical properties, improvement of the film quality is indispensable, and fundamental researches on growth mechanisms of adsorbed organic molecules are undertaken [4, 5]. In an experiment of pentacene (Pn, C$_{22}$H$_{22}$) growth on Si(001) [4], authors concluded that an organic thin-film growth is similar to the epitaxial growth of inorganic materials, such as the formation of fractal ramified islands like diffusion-limited aggregates (DLA) [4, 5].

On the other hand, in an experiment of Pn growth on a hydrogen-terminated Si(111) surface [H-Si(111)] [5], a peculiarity is found. On a flat H-Si(111) surface islands are compact with smooth edges and isotropic, whereas on a vicinal surface islands are dendritic in the step-down orientation while edges in the step-up orientation remain compact: Each island has a strong anisotropy in its shape on a vicinal substrate. Island shape anisotropy, however, is not specific to a vicinal surface. It is observed in the vapor growth of another organic molecule, a behenic acid, even on a flat singular substrate, namely on an oxidized GaAs [8]. In the present paper we analyze some model systems which lead to shape anisotropy theoretically.
II. 2D ISLANDS ON A FLAT SUBSTRATE

When molecules in a 2D crystal stack almost normal to a substrate surface but with a finite tilting, as to the a-axis in the case of a behenic acid \cite{8}, kinetics at island edges may depend on relative orientations of the edge and of the molecular tilting. To an edge where the molecular inclination restricts the incorporation space, diffusing molecules may be difficult to be attached to the edge, but once attached they may be difficult to be detached from this edge. Depression of the attachment rate slows down the incorporation kinetics, and the edge becomes smooth. On the contrary, suppression of detachment increases incorporation and leads to a diffusional instability of a smooth edge. So far the relation between the molecular tilting and the orientation of dendritic edge is not identified experimentally \cite{8}, we here assume simply that a molecular tilting affects detachment process such that the detachment rate of a molecule depends on the edge orientation. In our theoretical treatment, we forget about the finite size and shape of an adsorbing organic molecule, but consider it implicitly in the orientation-dependence of the detachment rate.

We perform kinetic Monte Carlo simulations \cite{19, 20} of a lattice gas models of point molecules depositing on a square substrate with a deposition rate \( F \) per area. Adsorbed molecules diffuse on a surface with a diffusion constant \( D_s \). When two diffusing molecules meet, they make a bond to lower an energy and form a cluster. Clusters enlarge their sizes by incorporating diffusing molecules at edges. On the other hand, molecules at edges can detach from the islands when they are loosely attached: Those particles with a single bond to the island can break the bond to migrate out on the substrate surface with a rate \( D_e \), but molecules with more than two bonds are assumed immobile. When a particle is deposited above an island, it diffuses on the island terrace till it reaches an edge, and steps it down to be incorporated into the island. Evaporation of adsorbed molecules from the surface is excluded, since the growth is assumed to take place at a low temperature. When there is no detachment, grown islands take a ramified dendritic form with irregular fine branches, similar to the DLA \cite{6, 5}. With a small detachment, one obtains dendritic aggregates with fat branches, as shown in Fig. 1(a). Here, parameters are \( D_s/F = 10^{12} \) and \( D_e/F = 10^4 \) with a system size \( L^2 = 500^2 \) and the coverage \( \Theta = 0.1 \). Although islands interfere with each other in a diffusion field, they have almost a symmetric shape. By applying the box-counting method, one obtains a rough estimate of the fractal dimension as \( d_f \approx 1.70 \).

We now introduce an anisotropy in the rate of detachment from edges. On the left edge of an island, for instance, we arbitrary reduce the rate of detachment by \( R_L \). Island morphology simulated by means of kinetic Monte Carlo simulation \cite{20} becomes anisotropic, as shown in Fig. 1(b) and 1(c). When the detachment from the left edge is reduced by a factor 10 as \( R_L = 0.1 \) (Fig. 1(b)), the left edges of islands grow faster than those in the other orientations, and the primary branch to the left extends about three times more than to the right. The fractal dimension by box counting remains the same value \( d_f \approx 1.7 \). On further reducing the detachment rate from the left edges to \( R_L = 0.01 \) (Fig. 1(c)), islands point sharply to the left with the left-to-right ratio ranging about 3 to 6, depending on environment. Primary branches extending to the left are fine and have less side-branches, compared to Fig. 1(a) and 1(b), and primary branches to other orientations have many secondary branches extending long to the left. Pointing structure leads to the small fractal dimension of \( d_f \approx 1.6 \) by the box-counting method. Island morphology in Fig. 1(c) looks quite similar to those observed for the behenic acid islands on an oxidized GaAs \cite{8}.

Instead of suppressing detachment from the left edge, the enhanced detachment from the right edge leads to anisotropic island shape \cite{19}. In this case, however, islands extend vertically in y direction, and the obtained shape looks different to what is observed in the experiment \cite{8}. On increasing the detachment rate \( D_e/F \), islands become more compact with smooth edges as a skeletal shape or even to a complete square. The effect of anisotropic detachment in these cases have been discussed previously \cite{19}.

III. ISLANDS ON A VICINAL SURFACE

We know consider the case of a heteroepitaxial growth on a vicinal surface, which might be relevant to Pn growth on H-Si(111) \cite{5}. On a flat terrace, Pn molecules form 2D islands, and they are compact with an isotropic shape. Therefore, Pn molecules might often detach from island edges. On a vicinal H-Si(111) surface, Pn islands show different morphology in the upward and downward directions relative to the substrate steps. Island edges extending to the step-down direction are pointed in a dendritic form, while those to the step-up directions remain to be smooth and round.

Since Pn is known to grow in a standing-up orientation
an interaction between Pn molecules is stronger than that between Pn and the substrate. Let us now imagine that a Pn crystalline film is growing on a vicinal surface with a positive slope, as shown in Fig. 2. When a film grows to the left in a step-down direction and reaches an upper side of the descending step, as a left island in Fig. 2, further crystal growth takes place by incorporating a Pn molecule from the lower terrace. In this case, the whole length of a newly attached molecule interacts with the island edge and the step ledge, and it is hard to be detached back to the lower terrace. Also, the free upper part of the long molecule may in general be susceptible to thermal fluctuation, and there may be a substantial entropy contribution which reduces the bonding free energy. Attachment from the lower terrace may lessen this entropy contribution and enhances the Pn-Pn bonding. Thus, the detachment rate from the lower terrace is diminished from the normal rate $D_e$ on a flat terrace by a factor $R_L < 1$ as to $D_e R_L$. On the contrary, when the island grows to the right in the step-up direction and reaches the lower side of the ascending step, as a right island in Fig. 2, the next Pn molecule to be incorporated is located on the higher terrace, and its upper part does not contribute to the Pn-Pn bonding. Since the substrate step has a height of about one fourth of the length of a Pn molecule, a loss in the bonding energy may be significant. Accordingly, those molecules incorporated into an island edge from the higher terrace are easily detached back to the higher terrace with an enhancement factor $R_H > 1$.

We now study the effect of this anisotropic detachment with rate modification factors $R_H$ and $R_L$ on the island morphology.

In kinetic Monte Carlo simulation of heteroepitaxial growth on a vicinal surface, steps are separated with a distance $L_s$. After a deposition, molecules perform $D_e/F$ times of diffusive migrations until a monolayer is covered, but during this period molecules collide to form clusters. Steps are assumed to have no effect on the surface diffusion, for simplicity. A large value of surface diffusion constant $D_e/F = 10^{15}$ is chosen in order to grow only a single island in our system of a size $L^2 = 500^2$. From edges of an island on a flat terrace, molecules with a single bond detach with a rate $D_e/F = 10^5$. Above a descending step, detachment is enhanced by a factor $R_H = 10$, but in front of the step detachment is assumed completely forbidden, $R_L = 0$, corresponding to an extreme case.

By initially providing an embryo of a size 2 by 2 at the center of the system, an island is nucleated and grows to the coverage $\Theta = 0.1$. As the step separation decreases from $L_s = 5$ to 2, the island shape alters as shown in Fig. 3(a) to 3(d). Even with a very large surface diffusion, a second island is nucleated accidentally in Fig. 3(c). At a large step separations $L_s = 5$ and 4, the island has only a weak left-right anisotropy, as in Fig. 3(a) and 3(b). When steps come closer as $L_s = 3$ and 2, anisotropy becomes obvious, as in Fig. 3(c) and 3(d).

In order to quantify the shape anisotropy, we measure the ratio $V_L/V_H$ of the front velocities to the lower side $V_L$ to the higher side $V_H$ as a function of the step separation $L_s$. A curve is a guide for eyes. The surface diffusion is $D_e/F = 10^{15}$ and the detachment rate is $D_e/F = 10^5$ with an enhancement factor to the uphill $R_H = 10$ and a complete suppression to the downhill $R_L = 0$.

So far, we discussed the shape of a single island. In a large area of the vicinal surface many islands are nucleated and they affect their mutual growth and shape through the diffusion field. In the Pn experiment one may identify some order in spatial arrangement of islands: Islands look to align in queues parallel to the tilting direction of a vicinal substrate, with a dendritic left edge of one island being contiguous to the smooth right edge of a left one. (See, for example, Fig. 2 (c) and (d) in Ref. [5].)
In our system with a limited size $L^2 = 500^2$, island density is controlled by varying the surface diffusion constant $D_s$. In some combinations of parameter values, simulation can produce island arrangements with some spatial ordering, as shown in Fig. 5. The height of the vicinal surface is increasing to the right with ascending steps at the separation $L_s = 2$. Molecules are deposited to the coverage $\Theta = 0.3$. The surface diffusion constant is set at (a) $D_s/F = 10^{10}$, (b) $10^{11}$, and (c) $10^{12}$. Other parameters are $D_s/F = 10^4$, $R_H = 5, R_L = 0$.

In order to evaluate spatial correlation explicitly, we calculated the correlation function

$$g(r) = \langle \sum_i n(r + r_i)n(r_i) \rangle / N \quad (1)$$

where the occupation variable $n(r_i)$ is unity when the lattice site $i$ is occupied by an admolecule, and zero when the site $i$ is empty. Since the system is periodic both in $x$ and $y$ directions with a periodicity $L$, the correlation function has the symmetry $g(x, y) = g(L - x, y) = g(x, L - y) = g(L - x, L - y)$. Thus, we obtained the height contour of $g(x, y)$ for $0 \leq x, y \leq L/2$, as shown in Fig. 6. A mark "H" represents the high hill-top with a strong correlation, and a mark "L" represents the low valley with a weak correlation. From Fig. 6(b) one clearly observes that the pattern has a strong periodicity with a period $p = (L/4, L/8)$ at a surface diffusion $D_s/F = 10^{11}$. With a smaller diffusion $D_s/F = 10^{10}$, average island density gets higher as in Fig. 5(a), and the periodicity is not commensurate to the system size. Therefore, $g(r)$ has a rather broad first peak around $r = (100,100)$ in Fig. 6(a). With a larger diffusion $D_s/F = 10^{12}$, there are a few islands as in Fig. 5(c), and $g(r)$ has a broad peak at around $r = (150,200)$.

So far, we discussed an extreme case with the step separation $L_s = 2$ in order to realize a strong anisotropic effect in our small system. Since the island shape anisotropy is expected to be caused by an accumulation of many weak anisotropy effect at steps, one has to pack as many steps in an island as possible. Actually, with $L_s = 3$ we can observe similar arrangement of many anisotropic islands, but with a larger separation $L_s \geq 4$, it becomes harder to observe anisotropy in islands. In a real system of Pn molecules, step separations are wider, 4.5nm to 10nm, but an island size is about 10µm and it spans many steps. It may be interesting if there is a critical size for an island to show a shape anisotropy.

**IV. SUMMAR Y AND DISCUSSIONS**

Motivated by heteroepitaxial growth experiments of long organic molecules on a flat or on a vicinal surface, effect of detachment anisotropy on the island shape is studied by means of kinetic Monte Carlo simulations of a lattice gas model.

Only with a molecular deposition followed by a surface diffusion, islands take a ramified dendritic shape, similar to DLA. Addition of detachment from the edge makes fat dendritic branches, and with a large enough detachment rate islands become compact in a square form.

If the long molecules are tilted in an epitaxial film, the rate of detachment from island edges may depend on the edge orientation. Simulation shows that the edge with a smaller rate of detachment shows diffusional instability and forms a dendritic tip. Resulting island shape looks similar to the one obtained in the experiment.

On a vicinal surface, an interaction between an edge molecule and a neighboring one depends on edge position. When an edge has just climbed up the substrate step, a molecular bonding is weak and an edge molecule may easily detach from the edge site. On the other hand, when an edge has just stepped down the substrate step,
a bonding is strong and the edge molecule is hard to detach. In our simulation we assume an extreme case of no detachment at a lower edge to stress an anisotropy effect. Simulations show clear anisotropy in adsorbed island shape as the step density increases.

In addition to the shape anisotropy of a single island, the orientation-dependent detachment rate may induce a spatial correlation in the arrangement of islands with clear peaks in the spatial correlation function. Since the random deposition process introduces shot noise in the nucleation process, a fast surface diffusion seems necessary to average out fluctuation and to induce a spatial order, but then the island separation becomes large. For further studies on spatial correlation, one needs a larger system size.

As for the reason of island shape anisotropy, one may think about a diffusional anisotropy, such that a step provides an asymmetry in an energy barrier for the admolecule diffusion. However, the asymmetric potential is unable to lead unidirectional motion nor a net drift, as the Feynman’s ratchet and pawl machine cannot provoke directional rotation \cite{21}. Another effect that steps may provide is a nucleation center by lowering the energy barrier. But in the experiment there is no observation of alignment of nucleation centers along the step direction. Therefore, the latter effect might be small. Observation of admolecule motion on the substrate, if possible, should resolve these points clearly.

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