Growth modes in two-dimensional heteroepitaxy on an elastic substrate

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Abstract

With the use of a two-dimensional harmonic elastic lattice model, in which spontaneous stress caused by the lack of neighboring atoms is incorporated, we determine ground state configuration of adsorbed atoms on a flat elastic substrate. Energy of the system is calculated by direct relaxation dynamics in the epitaxial layer and by using an elastic Green's function method in the substrate. Based on the ground state configurations determined for various coverages, we infer growth mode. As the lattice misfit and the strength of the spontaneous stress increase, the growth mode changes from Frank-van der Merwe(FM) to Stranski-Krastanov(SK) and finally to Volmer-Weber(VW) mode. In a parameter range between the SK and the VW with a large spontaneous stress, the equilibrium configuration changes from a layer to islands in unusual ways as the coverage increases.

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I.   INTRODUCTION

Elastic strain plays an important role in heteroepitaxial crystal growth [1, 2]. In order to release the strain due to misfit of the lattice constants between the substrate and the adsorbate, the adsorbate has a tendency to form three-dimensional islands instead of thin uniform layers. With a change of material parameters the adsorbate shows typically three different growth modes: the layerwise growth by wetting the underlying substrate completely, which is called Frank-van der Merwe (FM) mode; the three-dimensional island growth by wetting the substrate only partially, called Volmer-Weber (VW) mode; the island growth on a thin wetting layer, called Stranski-Krastanov(SK) mode. The most probable origin of the change of growth mode is the change of the equilibrium structure, *i.e.*, the lowest energy configuration, as a result of competition between the bond energy and the elastic strain energy. Theoretical prediction of the growth mode has been made with the use of the continuum elastic theory [3]. It has been shown, however, that the simple continuum theory [1] may not be accurate when the surface has a stepped structure as well as in a very small length scale [4, 5]. To avoid these difficulties we introduced a two-dimensional lattice model for the heteroepitaxial system and studied the effect of strain relaxation in the island [6] and the effect of the substrate elasticity [7]. The effect of the stepped structure is due to the spontaneous surface stress, which is naturally taken into account in our model. In the present paper we propose a qualitative growth phase diagram based on the energy calculation of our 2D lattice model.

In §2, we briefly explain our lattice model and calculation method for the heteroepitaxial system. In §3, we perform the energy calculation and find ground state configurations. We also infer the growth mode as a function of the lattice misfit and the spontaneous surface stress. In §4 we give a short summary and discussion.

II.   MODEL

We briefly describe our two-dimensional elastic lattice model, which is the same as the one used in [7]. The substrate and the adsorbate are assumed to form a square lattice coherently (Fig.1). The substrate is initially flat and the surface is a (01) face. The adsorbate forms a

complete atomic layer or islands on a complete layer. The potential energy of the system is the sum of nearest neighbor (nn) and next nearest neighbor (nnn) pair potentials, V_1 and V_2. It consists of nn and nnn bond energies, J_1 and J_2, and elastic energies due to the elastic force. The elastic forces occur as the position of the atoms are displaced from their original lattice points. The nn and nnn atomic forces at the original lattice points are σ_0 and $-\sigma_0/\sqrt{2}$. They are the first derivatives of the pair potentials (repulsive and attractive, respectively), and the factor $\sqrt{2}$ comes from a stability condition of the square lattice [4]. These forces cancel in the bulk and at the (01) surface, but produce a *spontaneous surface stress* at the steps if the surface is not flat, *i.e.*, if some of the neighboring atoms are absent. When an atom is displaced by $\boldsymbol{u}$ from a lattice point $\boldsymbol{m}$, the additional force

$$
\begin{aligned}
\boldsymbol{f} = K_1 &\sum_{\boldsymbol{\delta}_1}[(\boldsymbol{u}(\boldsymbol{m}+\boldsymbol{\delta}_1) - \boldsymbol{u}(\boldsymbol{m})) \cdot \boldsymbol{\delta}_1]\boldsymbol{\delta}_1 \\
&+ \frac{K_2}{2}\sum_{\boldsymbol{\delta}_2}[(\boldsymbol{u}(\boldsymbol{m}+\boldsymbol{\delta}_2) - \boldsymbol{u}(\boldsymbol{m})) \cdot \boldsymbol{\delta}_2]\boldsymbol{\delta}_2,
\end{aligned} \tag{1}
$$

arises, where $\boldsymbol{\delta}_1 = (\pm 1, 0)$ or $(0, \pm 1)$, $\boldsymbol{\delta}_2 = \pm(1,1)$ or $\pm(1,-1)$ are the nn and the nnn bond vectors that connect the nearest and the next nearest neighboring sites. For simplicity we assume the spring constants satisfy the condition $K_2 = K_1/2$, which makes the 2D square lattice elastically isotropic. In general the parameters J_1, J_2, σ_0, K_1 take different values for the substrate atoms, the adsobate atoms and between them. The natural lattice constant for a bulk material is different for the substrate and the adsorbate, a and b. The lattice misfit is defined by

$$
f = \frac{b-a}{a}. \tag{2}
$$

We first assign particular configuration for the adsorbate with the use of the lattice occupation variable $\{C(\boldsymbol{m})\}$ ($C = 1$ or 0), and make the system relax by the overdamped equation of motion.

$$
\frac{\partial \boldsymbol{u}(\boldsymbol{m})}{\partial t} = -\Gamma \frac{\partial U(\{C(\boldsymbol{m})\}, \{\boldsymbol{u}(\boldsymbol{m})\})}{\partial \boldsymbol{u}(\boldsymbol{m})}, \tag{3}
$$

where U is the total potential energy. When the harmonic lattice is relaxed, the total strain energy is given as a negative half of the product of the force $\boldsymbol{f}(\boldsymbol{m})$ exerting on the surface atoms and their displacement [1]:

$$
U_{\mathrm{el}} = -\frac{1}{2}\sum_{\boldsymbol{m}}^{\text{surface atoms}} \boldsymbol{f}(\boldsymbol{m}) \cdot \boldsymbol{u}(\boldsymbol{m}), \tag{4}
$$

where the sum is taken over only the atoms with missing neighbor. In order to accelerate the calculation we adopt an elastic Green's function formalism [7], in which the force $f_\alpha(\bm{m})$ acting on a substrate surface atom $(m_y = 0)$ from the whole substrate can be expressed in terms of the displacement of the surface substrate atoms as

$$f_\alpha^{\text{sub}}(m_x) = - \sum_{\beta=x,y} \sum_{m_x'=1}^{L} H_{\alpha\beta}(m_x - m_x')u_\beta(m_x', 0), \tag{5}$$

where L is the width of the system with a periodic boundary condition. Since the kernel function $H_{\alpha\beta}(m_x - m_x')$ can be calculated for the flat semi-infinite substrate, we can substitute the whole substrate by the single surface layer.

III.   NUMERICAL CALCULATION

We determine the minimum energy configuration of the adsorbate. In order to limit the freedom of atomic configurations, we calculate only the energies of layer configuration(**L**), island configuration(**I**) and island-on-layer configuration(**LI**) for integer monolyer coverages (Fig.2). The shape of the island is a trapezoid with the top and the base lengths $2l$ and $4l$, and the height l. This is a part of the Wulff shape for $J_2 = J_1/2$, which we take in our numerical calculation. The value of the parameters are the following: the lattice parameter of the substrate is taken as unity $(a = 1)$, the spring constants are the same for all species and $K_1 = 2K_2 = 2$, the bond energies of the adsorbate at their natural lattice spacing are $J_1 = 2J_2 = 0.1$. When the adsorbate forms a lattice coherently on the substrate, the bond energies are renormalized as [7]

$$\begin{aligned}
J_{1x} &= J_1 - \sigma_0 fa - \frac{1}{2}K_1(fa)^2, \\
J_{1y} &= J_1 + \frac{K_2}{K_1 + K_2}\sigma_0 fa - \frac{K_1 K_2^2}{2(K_1 + K_2)^2}(fa)^2, \\
J_2' &= J_2 + \frac{K_1}{2(K_1 + K_2)}\sigma_0 fa - \frac{K_1^2 K_2}{4(K_1 + K_2)^2}(fa)^2.
\end{aligned} \tag{6}$$

The *nn* forces are also renomalized as

$$\begin{aligned}
\sigma_{1x} &= \sigma_0 + K_1 fa \\
\sigma_{1y} &= -2\sigma_2 = \sigma_0 - \frac{K_1 K_2}{K_1 + K_2}fa.
\end{aligned} \tag{7}$$

The renormalized interface bond energies are assumed to be ten percent stronger than those of (6). This means that the adsorbate would wet the substrate completely if the elastic stress were absent. The calculated parameter range for the nn force is $0 \leq \sigma_0 \leq 0.3$ and that for the misfit is $-0.15 \leq f \leq 0.15$.

The energy of **L** can be calculated easily. Since the adsorbate is compressed horizontally, it expands vertically and takes the lattice constant c determined by the Poisson ratio. In **I** configuration an island consisting of N_i adatoms is placed in a system of length L with the periodic boundary condition. The system size L, the island size N_i and the coverage n_{cov} are related as $N_i = n_{cov}L$. In **LI** configuration an island is put on n_{layer} layers, and the adatom number N_a is related to other numbers as $N_i + n_{layer}L = n_{cov}L = N_a$.

Examples of the energy calculation are shown in Fig.3 for $\sigma_0 = 0.1$ and $f = \pm 0.1$. Potential energy per one adsorbate atom, U/N_a, is shown as a function of the number of island atoms N_i. These graphs indicate that the lowest energy configuration is **L** for one monolayer, **LI** for two and three monolayer coverage, and the optimum island size is infinity.

In this way we determined the lowest energy configuration for the coverage of one to three monolayers for various values of the strength of the spontaneous stress(the nn atomic force) σ_0 and the misfit parameter f. The result is summarized in Fig.4. In the figure we also indicate the approximate position of the boundaries of the different growth modes, which we infer from the ground state configuration. The nominal FM region **L** is very narrow, and we intensionally shift the line between FM and SK in the following way. Even if the lowest energy state is **LI**, we assign FM mode when the minimum island size to realize the ground state is more than one hundred. We did so because forming such a large nucleus to start the island growth is practically impossible due to the large energy barrier. The critical size one hundred is arbitrary and depends on the temperature in reality. Another point to be noted is that the most favorable island size is infinity in the **LI** region and finite in the **I** region for $f > 0$ while it is always infinite for $f < 0$ with the present parameter values.

From the growth mode diagram we see that FM, SK and VW modes appear as the absolute value of the misfit f increases, which is in agreement with [3]. In addition we find that the growth mode depends on the spontaneous stress σ_0, which operate in the same direction as $|f|$. There is an interesting region between SK and VW with large σ_0 for a compressed adsorbate ($f > 0$). In this region the tendency to form an island is strong. As the coverage increases, an island is formed at the cost of the pre-existing first layer. The

first layer is removed as the coverage increases, and rather unconventional growth modes may be seen.

As already mentioned, the phase daigram is by no means symmetric for the compressed adlayer ($f > 0$) and the streched one ($f < 0$). The most favorable island size is different and the position of the phase boundary is shifted. With $f < 0$ the transition region from SK to VW is very narrow and different morphology variation appears. The reason for the asymmetry is that the bond energy J and the nn force σ are renormalized differently by the linear terms in (6) and (7). The renormalization of the parameters in x direction is stronger because of the factor $K_2/(K_1 + K_2) = 1/3$. Then, roughly speaking, with $f > 0$ the bond energy is reduced and the elastic energy is enhanced compared to the original parameter values while the effect is the opposite with $f < 0$.

IV.   SUMMARY AND DISCUSSION

Our calculation clearly shows the effect of the misfit and the spontaneous stress on the heteroepitaxial growth mode. Increasing the misfit f and the spontaneous stress σ_0 both changes the growth mode from FM to SK, and further to VW. There is an interesting parameter region between SK and VW modes, where island growth occurs at the cost of pre-existing first layer. Since our model is two-dimensional, direct comparison to experiment is not possible. But the above tendency must be true in three-dimension and a few experiments [8, 9] indicate such a growth mode may actually occur.

To make the calculation of the lattice model more realistic and useful, it is necessary to find three-dimensional lattice Green's function and to include dislocations in the model. The progress in these directions is under way [10, 11].

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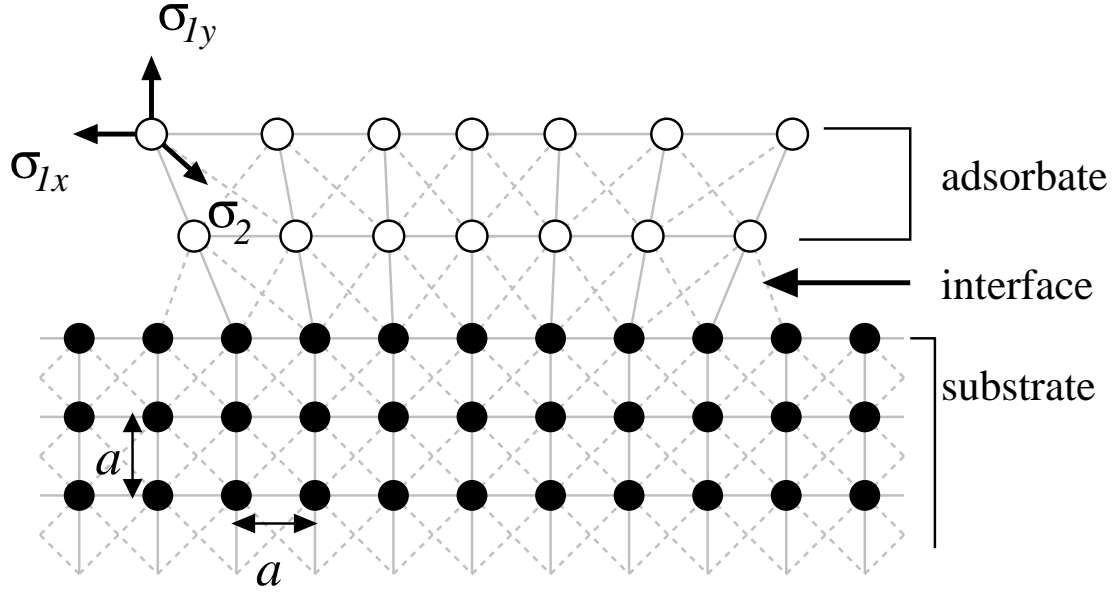
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FIG. 1: Two-dimensional elastic lattice model with spontaneous sress and a lattice misfit. Both the substrate and the adsorbate lattices can be deformed. (The figure is drawn for a rigid substrate.)
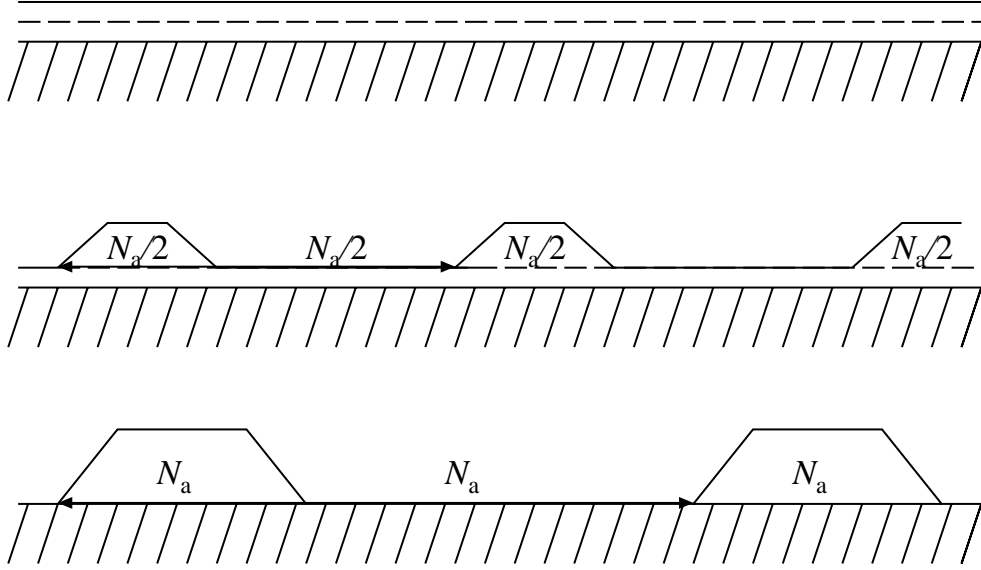
FIG. 2: Three kinds of adsorbate confugurations for two monolyer coverage: layer(**L**), island-on-layer(**LI**), island(**I**).
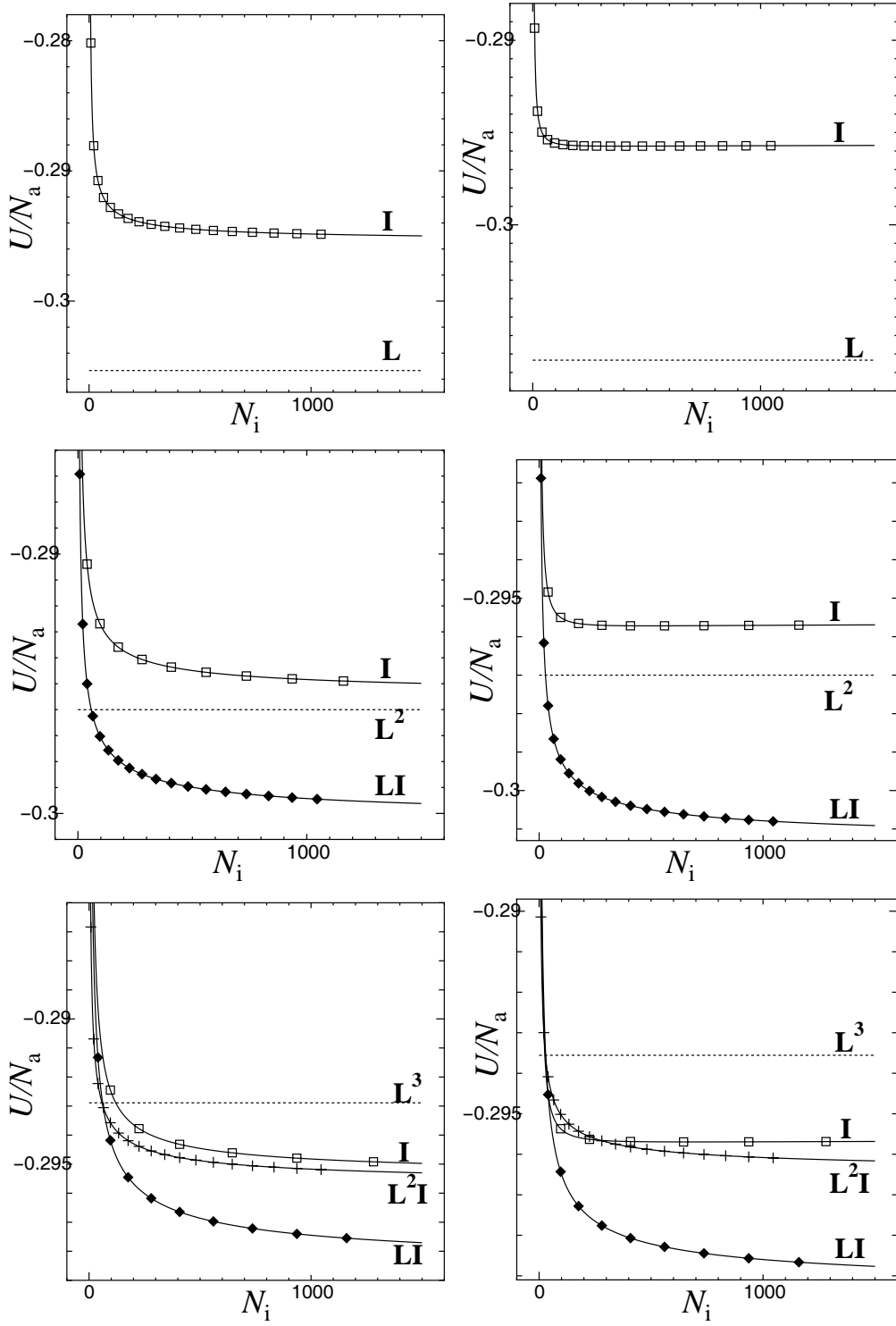
FIG. 3: Energy of different configuraions for the change of island size N_i. The coverage is one(top), two(middle) and three(bottom) monolayers. $\mathbf{L}$, $\mathbf{I}$, $\mathbf{LI}$, $\mathbf{L^2I}$ indicate a layer (or layers), an island, an island on a layer, an island on two-layers, respectively. The misfit parameter is $f = -0.1$(left) and $f = 0.1$(right).
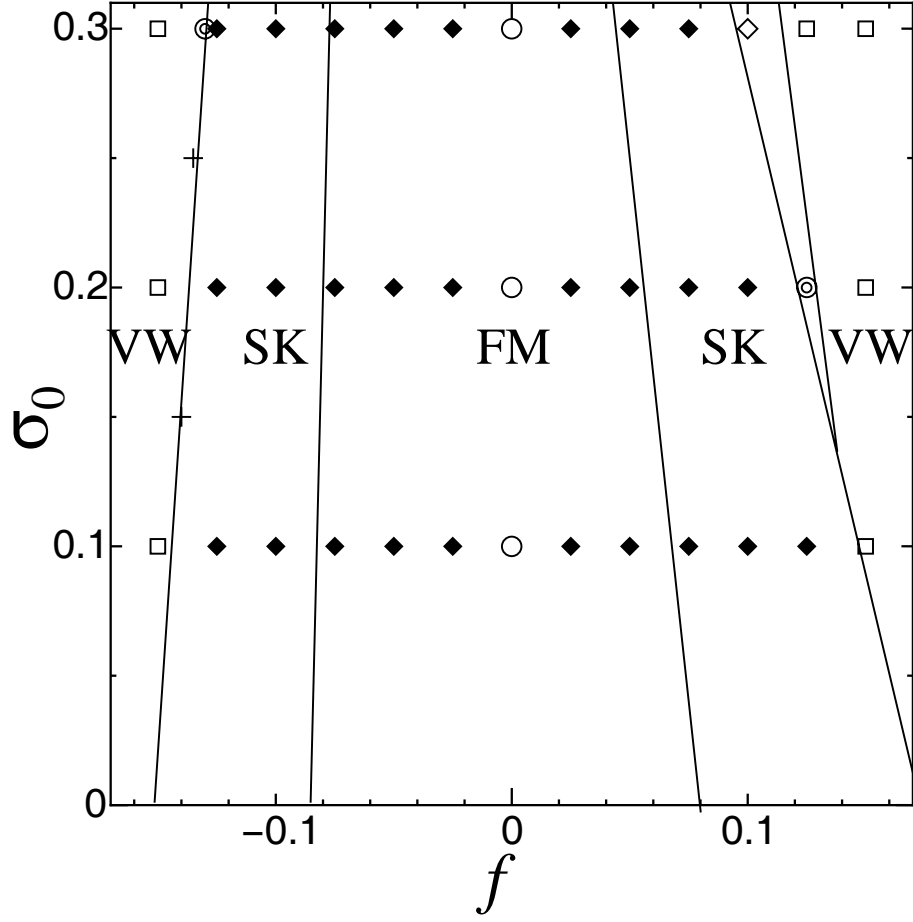
10

FIG. 4: Change of the ground state morphology for the change of coverage and inferred growth modes. The ground state morphologies are: circle $\mathbf{L} \rightarrow \mathbf{L}^2 \rightarrow \mathbf{L}^3$, filled diamond $\mathbf{L} \rightarrow \mathbf{LI} \rightarrow \mathbf{LI}$, square $\mathbf{I} \rightarrow \mathbf{I} \rightarrow \mathbf{I}$, double circle $\mathbf{L} \rightarrow \mathbf{LI} \rightarrow \mathbf{I}$, diamond $\mathbf{L} \rightarrow \mathbf{I} \rightarrow \mathbf{I}$, cross $\mathbf{I} \rightarrow \mathbf{I} \rightarrow \mathbf{LI}$.