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Relation between surface reconstructions and RHEED intensity oscillations

Makoto Itoh*
Interdisciplinary Research Centre for Semiconductor Materials, Imperial College, London SW7 2BZ, United Kingdom

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The effect of surface reconstructions on reflection high-energy electron diffraction intensity oscillations is examined by the Monte Carlo studies. It is pointed out that the double-periodic oscillations and the interchange of their peak intensities on semiconductor surfaces are accounted for by the effect of surface reconstructions. [S0163-1829(98)07832-1]

Reflection high-energy electron diffraction (RHEED) intensity oscillation has been widely used as an efficient technique to monitor surface growth phenomena during molecular beam epitaxy (MBE). For the interpretation of its time variation, the step density model (SDM) is often employed in association with the solid-on-solid (SOS) model, both of which have been applied to Si(001) and GaAs(001) surfaces.[1–3] Apparently this interpretation is not only consistent with RHEED intensity measurement but also with the scanning tunneling microscopy observation.[4]

However, the SDM has been applied to semiconductor surfaces only when each terrace has a singular and stable atomic structure and RHEED intensities show single-periodic oscillations (SPO's) on them.[5,2] For example, although a Si(001) surface has the (2×1) and the (1×2) structures in the alternative manner when a homoepitaxial growth proceeds in a layer-by-layer (LBL) fashion, we can observe only one of them on each terrace at once and not both. As for a GaAs(001) surface, although the definition of the SDM needs to be modified to sum up only terrace edges since the stable reconstruction is the $\beta 2(2\times 4)$ structure, which is composed of double hills and double trenches of As dimers running in the $[\bar{1}10]$ direction,[6–8] this structure is stable and continues to grow in a LBL fashion during homoepitaxy.[2] Therefore, as long as the SPO is observed, the SDM, or more precisely the combined use of the SDM and the SOS model seems to work well at least at a mesoscopic level.[9]

In general, however, there is a significant difference between a stable surface reconstruction and a bulk structure, between which a smooth pathway does not necessarily exist when either the change of unit cell's areas or that of atomic densities is involved. In such a case, a growth inevitably goes through a structural change between the bulk and the reconstructed structures and vice versa in a nontrivial way.

In order to study the effects of such transformations, let us consider a surface with several nondegenerate atomic structures. With some experimental conditions, RHEED intensities can be compared with the summation of all partial areas, each of which consists of a well-ordered periodic structure. This is opposed to the above case in which the summation of all the densities of areas of well-ordered structures on all terraces is, in the absence of surface defects, equivalent to the subtraction of a step density from unity, and this is why the SDM worked well. In other words, the SDM is applicable to a surface only when a singular stable structure dominates each terrace. In contrast, once multiple surface structures are involved, their domain boundaries will play a similar role as well, and thus the SDM does not simply apply as before. Therefore, it is necessary to consider a general growth phenomenon with the explicit introduction of a surface reconstruction.

For definiteness, let us denote the unit cell's area and the atomic density of ith phase ($i=1,2,3,\dots$) by S_i and μ_i, respectively, and assume the energy densities ϵ_i are in the increasing order of i while either $S_i \geqslant S_j$ or $\mu_i \leqslant \mu_j$ holds for $i<j$. Such a monotonic relation often arises when the effects of surface reconstructions play dominant roles on the stability of a surface.[10,11]

To exemplify this, we will consider the variant of the SOS model for which several transient structures as well as the stable reconstruction (SR) and the bulk-terminated (BT) structure are realized during a growth. Accordingly, when atoms are deposited onto a surface, it goes through a structural transformation from SR phases to BT phases via transient ones and vice versa so as to build a new atomic layer. In the model, the kinetic barrier of an atom at site $\mathbf{x}$ on the two-dimensional (2D) square lattice is defined by

$$E(\mathbf{x})=E_s+E_1\sum_{\mathbf{x}'\in\mathcal{N}_1(\mathbf{x})}\theta(h(\mathbf{x}')-h(\mathbf{x}))+E_2\sum_{\mathbf{x}'\in\mathcal{N}_2(\mathbf{x})}\delta_{h(\mathbf{x}),h(\mathbf{x}')},\tag{1}$$

where $h(\mathbf{x})$ denotes the height of an atom at site $\mathbf{x}$, whereas $\mathcal{N}_1(\mathbf{x})$ and $\mathcal{N}_2(\mathbf{x})$ stand for the sets of the nearest-neighbor (NN) sites and the next-to-NN sites of $\mathbf{x}$, respectively. The coefficients E_s, E_1, and E_2 denote the contributions to the kinetic barriers from the interactions with the substrate, with atoms in the NN sites of $\mathbf{x}$ provided their heights are larger than $h(\mathbf{x})$, and with top-layer atoms if their 2D coordinates are in $\mathcal{N}_2(\mathbf{x})$ and the heights are identical to $h(\mathbf{x})$. $\delta(x)$ stands for the Kronecker delta, and the Heaviside step function $\theta(x)$ is defined as unity if $x>0$ and zero otherwise. It is clear from Eq. (1) that for some parameter regions with $E_1<E_2$, the SR phase takes the checkerboard (CB) structure, with which some transient structures are also associated. Among them, the typical ones are the stretched checkerboard (SCB) structures as we will see in Fig. 2 below.

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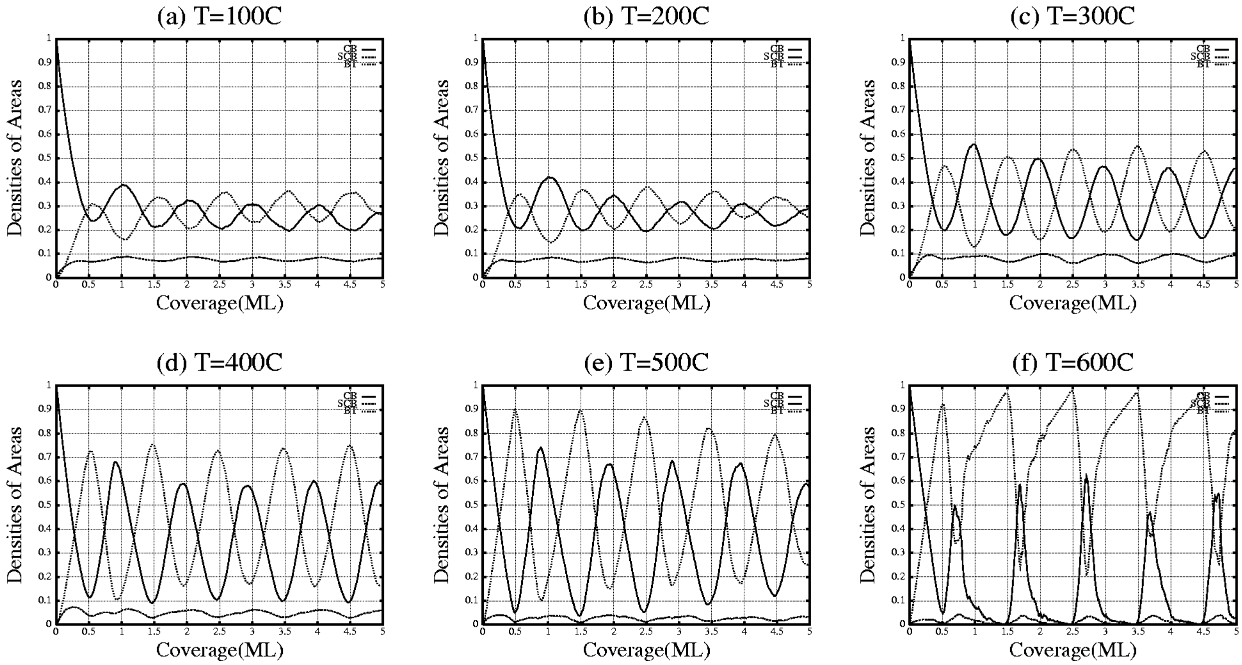

FIG. 1. Fractional areas of the CB, the SCB, and the BT phases are plotted as a function of a surface coverage. Calculations were done with $E_s = 1.3$ eV, $E_1 = 0.2$ eV, and $E_2 = 0.4$ eV. The lattice sizes are 120×120 for $T \leqslant 400$ °C and 80×80 for $T \geqslant 500$ °C, the maximum hopping length is 20, and the incident flux is 0.10 ML/s. (a) $T = 100$ °C, (b) $T = 200$ °C, (c) $T = 300$ °C, (d) $T = 400$ °C, (e) $T = 500$ °C, and (f) $T = 600$ °C.

The calculations are done by using the kinetic Monte Carlo algorithm[12,13] in which the rate R of a hopping event is given in terms of a barrier E by $R = \nu \exp(-E/k_BT)$, where $\nu = 2k_BT/h$, k_B is Boltzmann's constant, T is the substrate temperature, and h is Planck's constant.[14] The interaction parameters in Eq. (1) are set to $E_s = 1.3$ eV, $E_1 = 0.2$ eV, and $E_2 = 0.4$ eV, the incident flux is 0.1 ML/s, the maximum hopping length to search for a favorable site is 20, and the lattice sizes are 120×120 for $T \leqslant 400$ °C and 80×80 for $T \geqslant 500$ °C. The mean densities of the areas occupied by the CB phases, the SCB phases, and the BT phases are obtained by averaging over the intervals of every 0.1 s and are plotted in Figs. 1(a)–1(f) against a surface coverage of deposited atoms measured in units of monolayer (ML) thickness. We measure the surface densities of these three phases because they are the only common features to all temperatures.

The clear double-periodic oscillation (DPO) can be seen at $T = 400$ °C [Fig. 1(d)], below which the periodic structures are rather poorly developed. However, the peaks become sharper as the temperature is increased to reach $T = 500$ °C, and at $T = 600$ °C it becomes difficult to develop a well-ordered CB phase any longer. The two phases CB and BT interchange their peak intensities below and above $T \sim 300$ °C. This is seen especially at the initial stages of the growth. Also the peak positions due to the CB phases are shifted as the temperature is increased because at high temperatures the construction of new layers is more favored than to make a flat surface covered with the stable structures.

At a glance, it may look interesting that the oscillations due to the BT phases become asymmetric at $T \geqslant 500$ °C. However, this arises because the BT phase is free from any reconstructions, so that the only thing that is necessary for this phase to be developed is to capture deposited atoms. On a real semiconductor surface, in contrast, even at high temperatures a BT phase is not realized but some different metastable structures appear, so that a RHEED oscillation may remain rather symmetric as we can see in Refs. 15–17.

Some of the snapshots are shown in Figs. 2(a)–2(m), where we see several kinds of transient phases. Among them, we can easily recognize the SCB structures with the (6×2) periodicity in Figs. 2(a), 2(c), 2(e), and especially in the upper half of 2(g). We can also see the SCB structures with the (4×2) periodicity in the central part of Fig. 2(i) and in the lower-right corner of Fig. 2(k). Since the relations $\epsilon_{\rm CB} < \epsilon_{\rm SCB} < \epsilon_{\rm BT}$, $\mu_{\rm CB} = \mu_{\rm SCB} < \mu_{\rm BT}$, and $S_{\rm BT} < S_{\rm CB} < S_{\rm SCB}$ hold among three phases of our concern, the DPO must have resulted from the competition between the lowest ϵ_i structure and either the highest μ_i or the smallest S_i one.

Our results indicate the role a metastable structure may play on a RHEED intensity oscillation measurement of a semiconductor surface. For instance, the peak intensities of the DPO in Ge(111) homoepitaxy are found to interchange between low and high-temperature growth regimes,[15–17] and this is attributed to the competition between the stable $c(2\times8)$ and the metastable (2×2) surface reconstructions;[10] even other metastable structures might be involved. In fact, this mechanism was found to apply to a Si(001) surface on which the DPO was observed when the kinetic condition makes one of two alternative structures more favored than the other.[18,19] Its important feature is that the appearance of the DPO is insensitive to the glancing angles, which strongly indicates that this is due to the double degeneracy of the reconstructed structures.

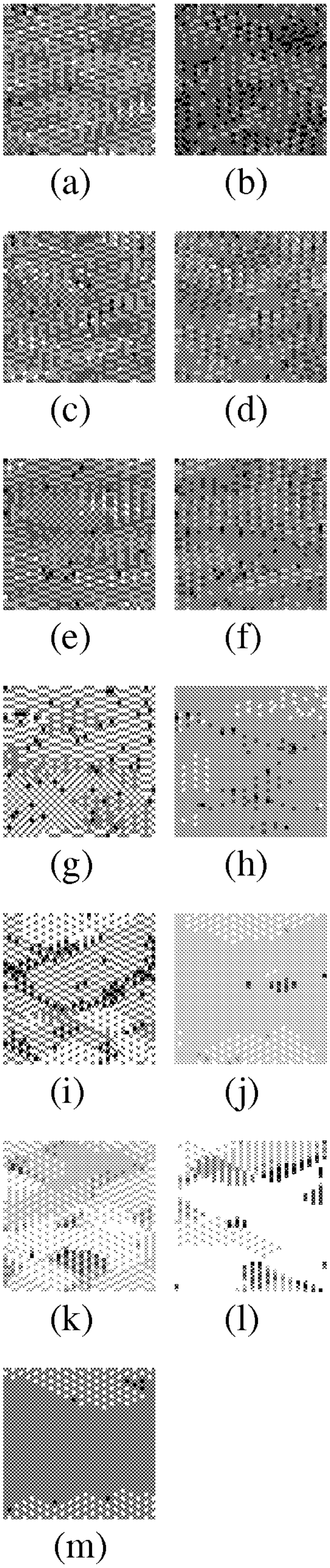

FIG. 2. Snapshots at several coverages. The higher, the brighter. (a),(b) $T=100$ °C: (a) 1.0 ML, (b) 1.5 ML. (c),(d) $T=200$ °C: (c) 1.0 ML, (d) 1.5 ML. (e),(f) $T=300$ °C: (e) 1.0 ML, (f) 1.5 ML. (g),(h) $T=400$ °C: (g) 0.9 ML, (h) 1.5 ML. (i),(j) $T=500$ ° C: (i) 0.9 ML, (j) 1.5 ML. (k)–(m) $T=600$ °C: (k) 0.7 ML, (l) 1.0 ML, (m) 1.5 ML.

This additionally implies that the RHEED observation of a GaAs(111) may show a DPO near the transition temperature between the $(2\times2)A$ and the $(2\times2)B$ reconstructions.[20,21]

However, this argument does not simply apply to a Si(111) surface, because the stability and the complexity of the (7×7) structure[22] makes its growth nature much different from others. For instance, the formation of this reconstruction is too complicated to keep up with the kinetic growth process, and hence a growing surface shows only locally ordered structures.[23,24]

Remarks on other works are in order. Some authors have tried to account for the DPO by the phase shift, which results from the interference between the topmost layer and the layer beneath.[25–27] However, none of them could have derived the temperature-driven interchange of the peak intensities of the DPO because their studies are not based on any microscopic dynamics.

As for the SDM, the criticism on it has been raised recently by Korte and Maksym, who treated an epitaxial layer coverage and a step density similarly as independent variables, and found that a RHEED intensity is an increasing function of a step density.[28] In general, however, a step density is not a variable but a quantity to be measured because it is a complicated function of a temperature, a crystallographic structure, and an atomic dynamics. Actually, their result contradicts with the RHEED intensity measurement of the Ge/Si(100) heteroepitaxy, where the onset of the three-dimensional islands, which means a sudden increase of the step density, was found to result in the rapid decay of the RHEED intensity.[29] The experimental support for the SDM has also been given by the direct measurement of a step density on the GaAs$(111)A$ surface.[30]

There arises the question that between the two mechanisms, namely the alternating dominance of the stable and the metastable surface structures and the conventional interpretation of the DPO by the interference between the topmost and the underlying layers, which one really contributes to the DPO of a RHEED intensity. If the feature of the DPO is sensitive to glancing angles, it may be attributed to the interference effect.[26] If not, on the contrary, the plausible mechanism is the effect of surface reconstructions, as is the case for the Si(001) surface.[19] Thus, presumably, the interference effect plays the central role on metal surfaces, while on semiconductor surfaces, the effects of reconstructions will play dominant roles. The easiest way to examine them is to carry out a RHEED intensity measurement for a solid surface and see (1) if one can observe the interchange of the peak intensities of the DPO when the temperature is changed, and (2) if the appearance of the DPO is sensitive to the change of a glancing angle.

In summary, the general relationship between surface reconstructions and RHEED intensity oscillations on semiconductor surfaces is pointed out. According to it, if the construction of a new layer via the LBL growth mode inevitably goes through the process of a surface reconstruction and its destruction in which either the change of unit cell's areas or the atomic densities is involved, the DPO behavior naturally appears in RHEED intensity measurement, which is associated with the interchange of their peak intensities as the temperature is increased. Also, our results suggest that the appearance of DPO itself results from the alternative dominance of the surface growth modes between the most stable structures and those having the property of either the highest atomic density or the smallest unit cell's area.

Recently, there appeared the article by W. Braun, L. Däweritz, and K.H. Ploog [Phys. Rev. Lett. **80**, 4935 (1998)] in which the relation between RHEED intensity and surface reconstructions is also discussed.

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*Electronic address: m.itoh@ic.ac.uk

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