Pyramid-Like Si Structures Grown on the Step Bunched Si(111)-(7×7) Surface

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Abstract – Pyramid-like Si structures have been observed on large (5 μm) atomically flat terraces of the step bunched Si (111)-(7×7) surface during Si deposition at T = 600°C–760°C in the ultrahighvacuum reflection electron microscope (UHV REM). Such structures are the result of sequential two-dimensional island nucleation and growth (2DNG) accompanied by reducing a terrace width after each monolayer formation. The critical terrace width, at which the next 2DNG layer starts, is measured depending on substrate temperature and Si deposition rate. Two different activation energies of 2DNG layer formation (E₂DNG) are found out: E₂DNG ≈ 2.4 eV at T < 700°C and E₂DNG ≈ 0.5 eV at T > 700°C. Based on experimental data a critical cluster size for 2D-island nucleation is determined to be 7–10 atoms.

Index Terms – Silicon, homoepitaxial growth, morphology, superstructure.

I. INTRODUCTION

The process of epitaxial 2D-islands nucleation on the atomically clean reconstructed Si(111)-(7×7) surface is the actual problem of surface science underlying “bottom-up” Si based nanotechnologies [1]–[3]. However, the growth on Si(111)-(7×7) surface is a complex phenomenon that involves a number of atomic scale processes like surface migration, the formation of stable nuclei, the incorporation of atoms into steps or 2D-islands. Many parameters characterizing these processes are hardly definable.

In epitaxial growth there is always competition between kinetic effects from the arrival of atoms onto the substrate and the surface tension forces, which drive the structure back to the equilibrium. The resulting morphology depends on a number of parameters including incident atomic flux, temperature and size of the feature of a substrate. Although growth on the vicinal surface has been well characterized [4], comparatively little work has been done on the effect of an incident Si flux onto the surfaces subjected to step bunching [5].

In this paper we present the study of the two-dimensional nucleation and growth of Si on the large (5 μm) atomically flat terraces of step bunched vicinal Si(111)-(7×7) surface. We observe a transition from attachment-detachment limited growth regime to diffusion limited one when sample temperature rises above 700°C at fixed silicon flux onto the surface.

II. PROBLEM DEFINITION

There are two basic mechanisms of crystal growth: step flow and two-dimensional island nucleation and growth (2DNG) [6]. The step flow mechanism is realized when substrate temperature is sufficiently high so that the migration length of adatoms is larger than the terrace width. The reduction of the temperature leads to the decrease of adatom diffusivity, which causes 2D-island nucleation and growth on the terraces. The interplay of surface diffusion and step attachment during the growth produces adatom concentration on terraces, which generally increases with increasing spacing between steps acting as sinks for adatoms. Consequently, a transition between step flow and 2DNG occurs also as the function of terrace width. This transition is characterized by a quantity called critical terrace width. Since growth consists of a number of thermally activated processes, the critical terrace width also displays an Arrhenius behavior as a function of deposition temperature [7], [8].

The major part of the studies connected with 2DNG on Si(111)-(7×7) surface has been performed by STM technique (see, for example, Refs. [9], [10]) which has significant restrictions on substrate temperatures and deposition rates. The typical temperature of a silicon sample is less than 500°C, and the typical silicon flux is less than 0.03 ML/s. This temperature range does not cover the whole interval of Si(111)-(7×7) structure existence which extends up to T = 830°C. Thus, there is some information deficit about processes taking place within the range T = 500°C–830°C.

We have studied layer-by-layer homoepitaxial growth on Si(111)-(7×7) surface at T = 600°C–760°C. In order to carry out experiments within this temperature range, we have used UHV REM. This technique provides in situ investigations of the structure and the morphology of a clean crystal surface at high temperatures (up to melting point). Furthermore, it is possible to obtain REM-images of the sample surface simultaneously with the change in temperature or substance flux onto the surface. UHV REM technique possesses the enough spatial resolution to observe a single monoatomic step with 0.314 nm height [11]. These possibilities allow us to observe and control the processes on crystal surfaces.

In this paper we report about the formation of new pyramid-like structures during homoepitaxial growth on...
Si(111)-(7×7) surface never observed before on the stepped vicinal Si(111) surface.

III. THEORY

The classical theory of 2D-island nucleation described in Ref. [12] picks out several stages of homoepitaxial growth. Firstly, atoms are deposited onto the surface and migrate on it. Then, diffusing adatoms meet each other and create clusters with different sizes. The theory supposes the existence of such a critical cluster size $i$ that clusters consisting of $i$ atoms and less are unstable and are possible to decay. The clusters, which contain more than $i$ atoms, are considered in this approach as stable and grow at the expense of adatom absorption forming thereby large 2D-islands.

Since neither STM nor UHV REM techniques can track adatom movements at sufficiently high temperatures, some indirect approaches are necessary for obtaining information about adatom diffusion, clustering and 2D-island nucleation. One of the widely used approaches was suggested by Venables et al. in Ref. [12]. The authors have derived an equation for the density of 2D-islands ($N_{2D}$) as function of crystal temperature ($T$) and atomic flux ($R$) being deposited onto the surface:

$$N_{2D} \propto R^\chi \exp \left( \frac{E_{2D}}{kT} \right),$$

where $k$ is the Boltzmann constant, $E_{2D}$ is the effective 2DNG activation energy, and $\chi$ is a scaling exponent. Ref. [12] provides an expression derived under the suppositions of no sublimation and sufficiently low energy barrier for the incorporation of an adatom into a 2D-island:

$$E_{2D}^l = \frac{E_i + iE_d}{i+2},$$

$$\chi = \frac{i}{i+2}. \tag{1}$$

Here $E_i$ is the activation energy for adatom surface diffusion, $E_i$ is the energy gain when $i$ single atoms join together and form a critical cluster (critical cluster binding energy). It is easy to see that $\chi$ is less than unity at every integer $i$. This theoretical approach has several extensions for the case of significant magnitude of the energy barrier for incorporation of adatoms into a monoatomic step [13], [14]. For example, in Ref. [14] the growth on the surface with the system of equidistant monoatomic steps divided by atomically flat terraces is considered. If steps are located close to each other, then the growth proceeds by step propagation. When the distance between steps is sufficiently large, the nucleation of 2D-islands takes place on almost the whole surface. The authors derive a general equation establishing linkage between minimal distance between steps $\lambda$, at which 2D-nucleation occurs, substrate temperature, deposition rate, energy barriers for incorporation of an adatom into ascending and descending steps, critical cluster size, critical cluster binding energy, adatom diffusion activation energy, and step permeability coefficient. When considering the growth limited by the incorporation of adatoms into monoatomic steps with the same energy barrier $E_b$ for adatom incorporation into steps at both sides of a terrace, the equation derived by the authors of Ref. [14] brings to this view:

$$\chi^2 \propto \left( \frac{1}{R} \right)^\chi \exp \left( - \frac{E_{2D}}{kT} \right), \tag{3}$$

$$E_{2D}^H = \frac{2E_i + iE_d + (i+1)E_b}{i+3}, \tag{4}$$

$$\chi = \frac{2i}{i+3}. \tag{5}$$

One can see that, when comparing expressions (2) and (5), in the latter case parameter $\chi$ is possible to be more than unity.

It is essential to note that if some reconstruction is present on growing surface, the energy barrier for the transformation of a reconstructed unit cell to a bulk structure $E_{sr}$ should be subtracted from numerators of formulae (1) and (4):

$$E_{2D}^l = \frac{E_i + iE_d - E_{sr}}{i+2}, \tag{6}$$

$$E_{2D}^H = \frac{2E_i + iE_d - E_{sr} + (i+1)E_b}{i+3}. \tag{7}$$

One can derive from formulae (6) and (7) an expression for $E_b$:

$$E_b = \frac{i+3}{2(i+1)} E_{2D}^H - \frac{i+2}{i+1} E_{2D}^l. \tag{8}$$
IV. EXPERIMENTAL RESULTS

1. Formation of Pyramid-like Structures

In Fig. 1 the series of consecutive REM-images illustrating the stages of pyramid-like structure formation is shown. First, cleaning of sample surface by high temperature annealing \( T \approx 1300^\circ C \) is performed by passing of alternating electric current through the sample. This process results in the formation of atomically clean Si(111) surface with the system of equidistantly spaced monoatomic steps. One can see the REM-image of this system in Fig. 1a. Single monoatomic steps are seen in this REM-image as lines of dark contrast; several of them are denoted by black arrows. The monoatomic steps are divided by regions of bright contrast which correspond to atomically flat singular sections of Si(111) surface being called terraces. During high temperature sublimation the monoatomic steps moved to the right. The terraces located in right part of Fig. 1a are therefore higher than the ones in left part.

When cleaning has been performed, annealing of the sample by passing of direct electric current is performed in such a way as to create step bunches – clusters of monoatomic steps [5]. Such step bunches are separated by wide atomically flat terraces with bright contrast. One can see in Fig. 1b REM-image of Si(111) surface with step bunches – wide dark stripes denoted by white arrows – divided by terraces with sizes about \( 3 \times 50 \mu m \). After the creation of step bunches, sample temperature is decreased down to the temperature necessary for an experiment. For example, in Fig. 1b the surface is at \( 600^\circ C \).

When silicon deposition starts, two-dimensional growth islands (one of them is circled in Fig. 1b) begin to nucleate and grow in the central part of the singular region. The further deposition with rate \( 1.5 \cdot 10^{-3} \) ML/s (1 ML = 1.56 \( \cdot 10^{15} \) cm\(^{-2} \)) leads to the increase in island quantity and their lateral sizes, and after 80 seconds their REM-image exhibits a wide stripe of speckled black-and-white contrast (Fig. 1c). Similar regions with the nucleation of islands having monoatomic step height are circled in Fig. 1c-e. One can see that there are bright contrast sections free from islands near step bunches. These re-
gions are known in the literature as depletion zones. The appearance of these zones is explained by the drain of non-equilibrium adatoms to step bunches and monatomic steps, and the width of the depletion zone $L_{dep}$ is proportional to the migration length of an adatom at given temperature and deposition rate.

The further silicon deposition leads to the coalescence of islands, which results in the formation of a new two-dimensional layer (with the monoatomic step height) bordered by two monoatomic steps directed towards opposite directions. REM-image of this 2D-layer at the moment when nucleation of 2D-islands of a new layer occurs is shown in Fig. 1 d. One can see a dark wave-like stripe marked by black arrow near the step left bunch, which corresponds to a newly formed monatomic step on the left. There is also near the right bunch (denoted by letter A in Fig. 1d) a region with the contrast darker than the images of terraces but brighter than the images of monoatomic steps. This is a region, where the annihilation of steps takes place. One of annihilating steps has separated from the right step bunch during homoepitaxial growth, and the second one is the edge of the mentioned 2D-layer.

When the substrate temperature and silicon deposition rate are constant, the morphology of this structure modifies periodically. After 2D-island nucleation atop the highest 2D-layer and their enlargement, the coalescence of the islands occurs. This process results in formation of a new top 2D-layer and a pair of monoatomic steps bordering it. The further deposition of silicon is followed by the displacement of these steps towards the step bunches in opposite directions. This motion proceeds until the terrace width of the new top layer reaches a critical value $W_{crit}$. When this value is overcome, 2D-islands of a new 2D-layer appear in its central part. After that the process repeats, and the steps continue to move towards opposite directions. In the sequel one of them will incorporate into a lower step bunch, and the second one will annihilate with the step from an upper step bunch. It has been determined after the series of experiments that the period 2DNG at a top 2D-layer is equal to the time of one monolayer deposition onto the surface.

One can note that both depletion zone width $L_{dep}$ and critical width of 2D-layer $W_{crit}$ are proportional to the migration length of an adatom during homoepitaxial growth. Generally, the increase of silicon deposition rate resulted in the diminishing of $L_{dep}$ and $W_{crit}$. This fact caused the decrease of the distance between steps separating different 2D-layers $D_{step}$. The enhancement of deposition rate enables thereby to increase the number of 2D-layers between bunches and to create structures resembling in a cross section like pyramids. For example, REM-image of such a pyramid-like structure at $T=600^\circ C$ and $R=10^{-^2}$ ML/s is present in Fig. 1e. This structure consists of three 2D-layers with monoatomic step height, and the highest one has a 2DNG region.

The dependence of critical terrace width $W_{crit}$ on temperature and deposition rate was measured during in situ experiments. The values of $W_{crit}^2$ were used as the analog of 2D-island density $N_{2D}$ being traditionally measured by STM because both $W_{crit}^2$ and $N_{2D}$ are proportional to the adatom surface migration length ($W_{crit}^2 \propto \lambda_m^2 \propto N_{2D}^{-1}$).

2. Dependence of Critical Width on Growth Parameters

The experimental dependences of $W_{crit}^2$ on temperature at different silicon deposition rates are plotted in Arrhenius coordinates in Fig. 2 a. One can extract the effective 2DNG activation energy $E_{2D}$ from the slope of the exponential part of approximation (3). It is clearly seen that all of the plots for fixed deposition rate possess the change of the slope at temperatures above $700^\circ C$: $E_{2D} = 2.4\pm 0.1$ eV and $E_{2D} = 0.5\pm 0.2$ eV in low- and high-temperature ranges, respectively.

Fig. 2. Experimental dependences of $W_{crit}^2$ on temperature (a) and silicon deposition rate (b) fitted by expression (3).

In Fig. 2 b the dependences of $W_{crit}^2$ on silicon deposition rate onto the surface at different substrate temperatures are presented. According to rate equation theory discussed above, these data are supposed to be fitted by the power part of approximation (3). One can see that plots have sections with the same slope corresponding to the scaling exponent $\chi \approx 1.46$.

V. DISCUSSION OF RESULTS

We have obtained scaling exponent $\chi = 1.46\pm 0.10$ during experiments with measuring $W_{crit}^2$ when varying deposition flux at fixed temperatures. The values of $\chi > 1$ indicate usually that growth proceeds under the kinetic limitations of adatom incorporation into monoatomic step.

The application of formula (5) to the obtained value of $\chi$
yields the quantity of atoms in a critical nucleus. It consists of 7–10 atoms.

One can see that the low-flux dots of the 720°C plot in Fig. 2b does not fall under power approximation with $\chi \approx 1.46$. This observation authenticates the modification of growth regime which seems to be removal of the kinetic limitations of adatom incorporation into a monoatomic step at high temperatures. This hypothesis allows us to estimate the magnitude of the energy barrier for adatom incorporation into a monoatomic step at high temperatures. This hypothesis allows us to estimate the magnitude of the energy barrier for adatom incorporation into a monoatomic step from the modification of $E_{2D}$ observed in Fig. 2a. Since the top 2D-layer of a pyramid-like structure is bordered by only a descending step, one can estimate $E_b$ for the incorporation of adatom into a descending step under supposition of impermeable steps. From the substitution of parameters by values $i = 8$, $E_{2D}^{\perp} = 2.4\,\text{eV}$, and $E_{2D}^{\parallel} = 0.5\,\text{eV}$ into formula (8), one can obtain $E_b \approx 0.9\,\text{eV}$.

### VI. CONCLUSION

The dependence of critical terrace width $W_{crit}$ on temperature and flux has been measured during in situ UHV REM study of Si growth on large (5 μm) atomically flat terraces of the step bunched Si(111)-(7×7) surface. It is shown that due to large terraces the only 2DNG-mode is realized at $T = 600^\circ\text{C} – 760^\circ\text{C}$. We find out that the dependence of $W_{crit}$ on silicon flux exhibits a power law with scaling exponent about 1.46, which corresponds to the critical nucleus consisting of eight atoms. From the slope of $W_{crit}(T)$ plotted in Arrhenius coordinates, it is found out that effective 2DNG activation energy $E_{2D}$ equals to 2.4 eV and 0.5 eV for temperatures below and above 700°C, respectively. In accordance with the theory presented by B. Rangelov, M. S. Altman, and I. Markov in Ref. [14] this abrupt change of activation energy $E_{2D}$ is caused by transition between diffusion and attachment-detachment limited growth regimes. This yields the estimate of the energy barrier for adatom incorporation into a descending monoatomic step $E_b \approx 0.9\,\text{eV}$.

### REFERENCES


