Nano-Texturing of Surface by Constricting Epitaxial Growth of Molecules

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Abstract
This paper discusses the application of Molecular Beam Epitaxy (MBE) process to texturing. In this process, silicon molecules grow laterally along specific crystal planes of silicon substrate under a specific condition. It was found that an array of pre-processed holes produces texture because it constricts these lateral growths to specific directions on the substrate and forms three-dimensional regular shapes. This paper clarifies the mechanism and the design of texturing. Depending on the design of hole array, various textures are produced. The geometrical limitation and attainable accuracy are also discussed.

Keywords:
Nano-texture, Physical vapor deposition(PVD), Single crystal silicon

1 INTRODUCTION

Textured surfaces with nanometer scale and ultra fine periodic three-dimensional structures can bring many excellent functions and are expected to be applied for various applications [1]. So far, various processes have been adopted to produce textured surface such as cutting [2], laser processing [3], anisotropic etching [4] and so on. However, there is not any proper process that can satisfy the higher requirement for the pitch and shape of the texture that is necessary in future. Although Focused Ion Beam process [5] can produce fine structure in nanometer scale, three-dimensional structure is difficult to produce as well as the productivity is limited.

Molecular Beam Epitaxy (MBE) is one of the crystal growth technologies and can produce regular structure that consists of specific crystal planes with atomically smooth surface [6, 7, 8]. The principle of form generation is not the copying rule but strongly affected by the regularity of crystal, thus, good geometrical accuracy is expected. In specific condition, silicon molecules grow laterally along specific crystal planes of silicon substrate and form triangular cross section. An array of pre-processed holes can produce texture because it constricts these lateral growths to specific directions and forms three-dimensional regular shapes. The growth thickness is precisely controllable because step-flow, namely, layer-by-layer deposition is possible. Thus this process is expected to provide the texturing in nanometer scale.

This paper clarifies the principle or mechanism of this texturing, then discusses a design procedure together with geometrical limitation. Finally, the attainable accuracy is discussed.

2 CONSTRICTION OF STEP-FLOW GROWTH

Figure 1 shows an example that suggests a possibility of the texturing. This is the case of homo-epitaxy, that is, single-crystal layers are grown on a single-crystal silicon substrate. Tuning the conditions of epitaxial growth on (111) substrate, the growth becomes step-flow mode, namely, layer-by-layer mode. In this case, the growth is initiated from the step-end of each atomic layer. The step-ends are distributed uniformly on the substrate, because typical substrates have miss-orientation and the crystal facet is not same with the specified one. Thus, in this figure, many steps are observed on the grown surface. The direction of the lateral growth is along the orientation of $[2\bar{1}\bar{1}]$. In addition, several steps of the growth layer get together or bunched, and the spacing of the steps becomes almost constant. This mean-step-spacing is affected by the magnitude of miss-orientation and the conditions of epitaxial growth. In this case, it was about 1μm as shown in the figure.

In the middle of the surface, there is a small hole made by the pre-processing. It can be seen that the step-flow growth is constricted at the edge of this hole and the specific facets remain. These facets are identified as [11

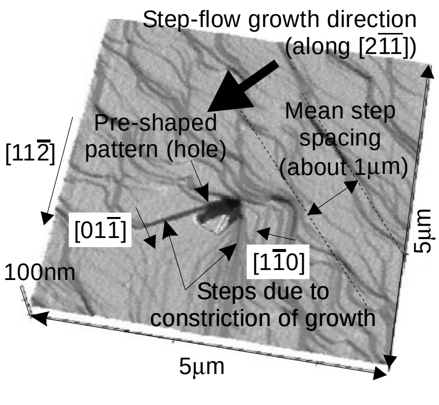


Figure 1: Example of step-flow growth and constriction observed by Atomic Force Microscope (AFM).

0] and $[01\bar{1}]$. The surface energy of these facets is one of the smallest, thus this result is considered as reasonable.

Figure 2 shows the schematic model of the texturing by MBE with pre-processing. Considering two directional miss-orientations, the shape of the growth layer becomes a triangular pyramid. This pyramid is considered as an energy-minimum body because it consists of facets that have minimum surface energy. The two facets of these are constricted by the pre-processed pattern, a hole in this study.

Setting the pre-processed pattern in an array, regular texture can be produced. In the figure, two types of setting are shown. By changing the pitch of pre-processed holes, the spacing of the texture shape is changed. Also, by changing the offset angle from the specified orientation, the top-view of the texture shape becomes isosceles or scalene triangle because the facets of the sidewall of the texture are determined as $[1\bar{1}0]$ and $[01\bar{1}]$. The parameters that affect the texture shape are listed below.

Diameter of hole	D
Pitch of holes	P
Offset angle (from specified orientation)	θ
Miss-orientation	α, β
Mean step spacing	S

The last parameter S is difficult to control because it is affected both the miss-orientation of the substrate and the conditions of epitaxial growth.

3 EXPERIMENTAL SETUP AND PROCEDURE

Figure 3 shows the procedure of texturing. Electron-beam lithography was used to draw circular patterns on the resist. Shallow holes were etched on the substrate using Reactive Ion Etching (RIE). After the removal of resist and cleaning, MBE process was carried out. The conditions of MBE process were set to keep the step-flow mode [7]. The set-up and the procedure of RIE and MBE are the same as the references [6, 7, 9]. The texture was observed by Atomic Force Microscope (AFM).

Table 1 shows the specification of substrate, the conditions of RIE and MBE processes, and the specification of pre-patterned holes. The substrate is commercially available (111) single-crystal silicon wafers cut from the same ingot. The depth of pre-patterned holes was kept constant at 35nm in all experiments.

It was confirmed that the growth layer had a single crystal (111) structure, same with the substrate, by analysing Reflection High-Energy Electron Diffraction (RHEED) pattern just after the MBE process. Also, it was confirmed that RIE left no severe surface damage that affect the MBE process.

4 EXPERIMENTAL RESULTS

4.1 The effect of the pre-pattern size

Figure 4 shows the effect of the pre-pattern size on texturing. The diameter of holes D and its pitch P were varied as shown in the figure while keeping the ratio P/D at constant. When the pre-pattern size was as small as the mean step spacing S (1μm in this case), as shown in Figure 4 (a), the growth layers were well constricted

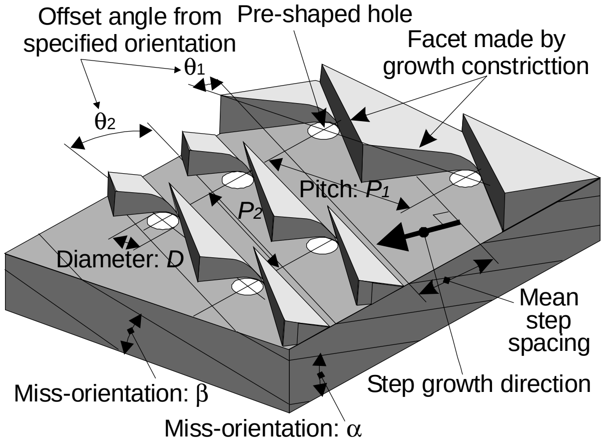


Figure 2: Model of texturing by MBE.

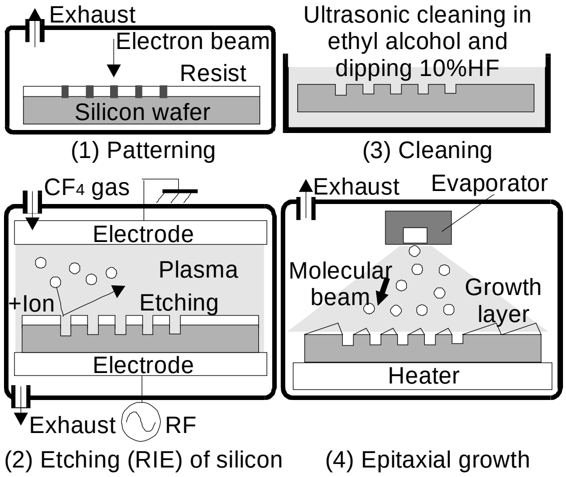


Figure 3: Processes for texturing.

Substrate	Orientation	(111)
	Size	ϕ50mm, t450μm
	Miss orientation	2deg. toward $[2\bar{1}\bar{1}]$
Pre-processing (RIE)	Diameter D	1, 2, 5[μm]
	Pitch P	1.5, 2, 2.5, 3[μm]
	Offset angle θ	0, 30, 45[deg]
	Depth H	35[nm]
	Gas, Pressure, processing time	CF_4, 6.7[Pa], 300[s]
Epitaxial growth process	Substrate temperature	1073[K]
	Growth rate	0.05[nm/s]
	Grown thickness	180[nm]

Table 1: Experimental conditions.

and the texture pattern was clear. However, when the pre-pattern size became larger, the texture pattern became dim because the constriction of the growth became weakened as shown in Figure 4 (b). In Figure 4 (c), mean-step-spacing was observed on the whole surface including the bottom of the hole. It is found from these results that the small pre-pattern size is preferable and the diameter of holes D should be smaller than the mean step spacing S for texturing.

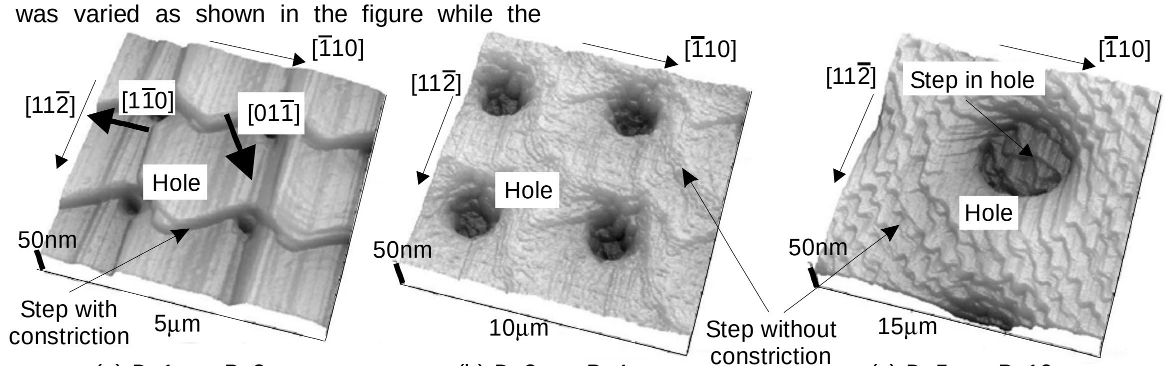
4.2 The effect of the pitch of holes

Figure 5 shows the effect of the pitch of holes P on texturing. In this case, the pitch of holes P was varied as shown in the figure while the diameter of holes D was kept at constant 1μm. When the pitch P was 1.5 and

2µm, clear triangular texture pattern with $[1\bar{1}0]$ and $[01\bar{1}]$ facets was observed. However, when the pitch *P* was 3µm, the texture pattern became dim or random. It is also found from these results that the pitch of holes *P* should be smaller than the mean step spacing *S* for texturing.

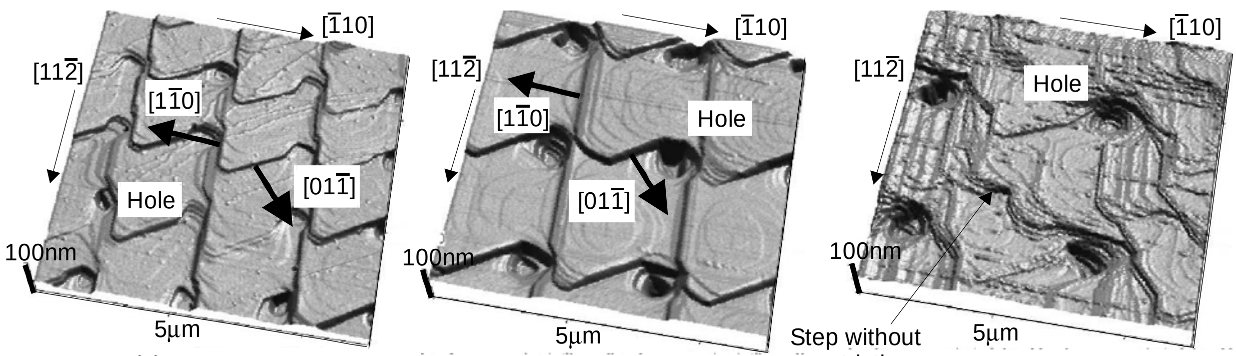
4.3 The effect of the offset angle of hole array

Figure 6 shows the effect of the offset angle θ on texturing. The offset angle θ, defined as the angle from $[11\bar{2}]$, was varied as shown in the figure while the diameter of holes *D* and its pitch *P* were kept at 1µm and 1.5µm, respectively. In all cases, clear triangular texture pattern with the height of several tens nanometers was obtained, however, the length of two sides of the pattern was different depending on the offset angle θ. The reason is that the intersection of two facets was varied while the angle θ between the two sides is always constant because the two sides consist of constricted steps of $[1\bar{1}0]$ and $[01\bar{1}]$ directions. This is one of the limitations of this texturing process.



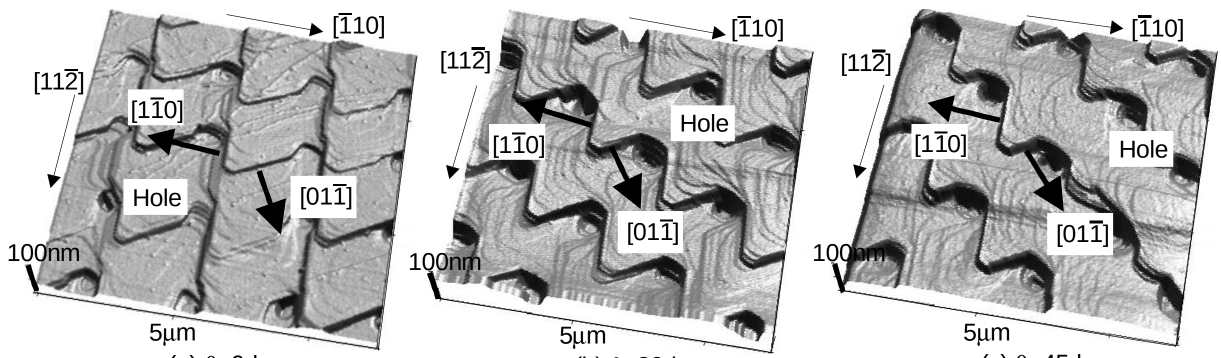
(a) *D*=1µm, *P*=2µm (b) *D*=2µm, *P*=4µm (c) *D*=5µm, *P*=10µm

Figure 4: Effect of the pre-pattern size (θ=0deg.).



(a) *P*=1.5µm (b) *P*=2µm (c) *P*=3µm

Figure 5: Effect of the pitch of holes (*D*=1µm, θ=0deg.).



(a) θ=0deg. (b) θ=30deg. (c) θ=45deg.

Figure 6: Effect of the angle θ (*D*=1µm, *P*=1.5µm).

5 DESIGN OF TEXTURE

The experimental results have proved that an array of holes constricts the step-flow growth and forms the textured surface with nanometer scale. Various textures can be obtained under some limitations by changing the pre-pattern. In the following, a design procedure is discussed.

Figure 7 shows the design procedure of texture.

Step 1: To determine the substrate orientation so that the step growth direction and its spacing *S* are the specified ones based on the geometry of crystal structure.

Step 2: To determine the diameter of holes *D*, its pitch *P*, and the offset angle θ on the basis of "*D*<*S* and *P*<*S*".

Step 3: To draw the tangential lines along the crystal direction $[1\bar{1}0]$ and $[01\bar{1}]$ from the edge of the holes. The intersection of these lines becomes the profile of the texture.

By changing the offset angle θ, the ratio of the side's lengths of triangular pattern can be changed. In other words, this process provides flexibility in the design.

Figure 8 shows the results of wide-area observation of texture. It shows the appearance of the 30μm by 30μm area where the diameter of holes *D*, its pitch *P* and offset angle θ were 1μm, 1.5μm and 0degree, respectively. It is found from the cross-sectional observation that regular texture pattern was obtained over wide area and the inclination angle of the triangular shape was almost constant with the height of 20nm. However, the top or bottom of the triangle was not at the same height.

Figure 9 shows the appearance and the cross-section of the pre-patterned holes. The cross-section was almost rectangular shape with the height of 35nm, however, the height of the bottom had fluctuation in nanometer order. This fluctuation, of course, affects the results of the accuracy after the epitaxial growth. Thus, it is important to keep high accuracy in the pre-processing to obtain the accurate texture.

6 CONCLUSIONS

It was made clear that the step growth can be constricted by an array of pre-patterned holes forming nano-texture in homo-epitaxy of silicon (111) substrate. The results are summarized as follows:

(1) The top view of the texture obtained in this study became triangular shape which consisted of $[1\bar{1}0]$ and $[01\bar{1}]$ facets**.**

(2) The diameter of pre-patterned holes *D* and its pitch *P* should be smaller than the mean step spacing *S* to obtain a desired texture. In this study, it was about 2μm.

(3) The texture which has arbitrary triangular shape can be obtained if the offset angle θ is selected suitably.

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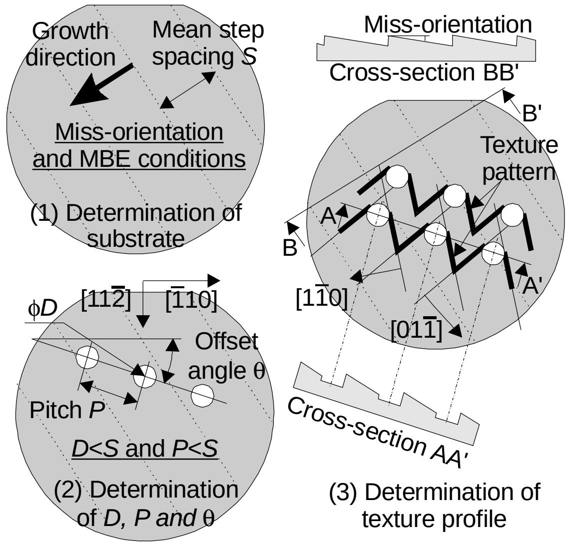

Figure 7: Design procedure of texturing.

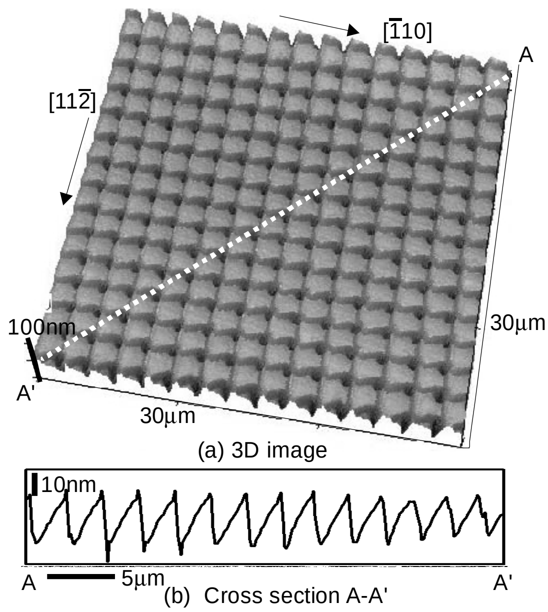

Figure 8: Example of textured surface (*D*=1μm, *P*=1.5μm, θ=0deg.).

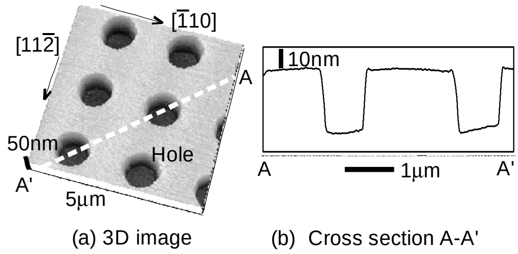

Figure 9: Example of pre-shaped holes (*D*=1μm, *P*=1.5μm, θ=0deg.).