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SEMICONDUCTOR STRUCTURES, LOW-DIMENSIONAL SYSTEMS, AND QUANTUM PHENOMENA

Nucleation of Two-Dimensional Islands on Si (111) during High-Temperature Epitaxial Growth

S. V. Sitnikov[a]*, S. S. Kosolobov[a,c], and A. V. Latyshev[a,b]

[a] *Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, Novosibirsk, 630090 Russia*
[c] *Skolkovo Institute of Science and Technology, Moscow, 143026 Russia*
**e-mail: sitnikov@isp.nsc.ru*

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Abstract—The process of two-dimensional island nucleation at the surface of ultra large Si (111) during high-temperature epitaxial growth is studied by in situ ultrahigh-vacuum reflection electron microscopy. The critical terrace size D_{crit}, at which a two-dimensional island is nucleated in the center, is measured in the temperature range 900–1180°C at different silicon fluxes onto the surface. It is found that the parameter D_{crit}^2 is a power function of the frequency of island nucleation, with the exponent $\chi = 0.9 \pm 0.05$ in the entire temperature range under study. It is established that the kinetics of nucleus formation is defined by the diffusion of adsorbed silicon atoms at temperatures of up to 1180°C and the minimum critical nucleus size corresponds to 12 silicon atoms.

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1. INTRODUCTION

Atomic mechanisms of the formation of the surface morphology of silicon crystals during homoepitaxial or heteroepitaxial growth are extensively studied in the context of the wide use of molecular-beam epitaxy in semiconductor nanotechnologies. During layer-by-layer homoepitaxial growth, growth can proceed via two different mechanisms, the two-dimensional (2D) island mechanism and the step-layer mechanism, depending on temperature, the degree of oversaturation at the surface, and the sizes of singular terraces between atomic steps.

The 2D island mechanism of growth at the vicinal Si (111)-(7 × 7) surface was studied by different experimental techniques: scanning tunneling microscopy [1], slow-electron microscopy [2], scanning electron microscopy [3], etc. [4]. The fundamental parameters describing the diffusion of adsorbed atoms (adatoms) and their interaction with atomic steps on the surface were determined [5, 6]. However, at present, there are practically no published data on the processes of nucleus formation at the Si (111)-(1 × 1) surface.

This is because of the fact that, as the substrate temperature is increased at constant oversaturation at the surface and a constant spacing between atomic steps, the 2D island mechanism of growth converts to the step-layer mechanism and the process of nucleus formation ceases. The change in mechanisms is caused by an increase in the migration length of atoms adsorbed at the surface because of more intense surface diffusion. Specifically, it was shown [7] that, at a temperature of 870°C, the critical terrace size, at which the mechanism of growth at the Si (111) surface changed, was 2 μm (at deposition rates of silicon of 0.3–0.6 monolayers (ML) per second). Such a terrace size corresponds to misorientation of the substrate from the (111) crystallographic face by an angle of ~0.01°. To study the processes of 2D island growth at elevated temperatures, it is necessary to produce singular terraces larger in sizes.

In this study, we propose the method of fabricating silicon substrates with areas containing atomically smooth wide singular terraces (up to 200 μm in dimensions) arranged at the tops of specially formed pedestals. This allowed us to study the processes of 2D island nucleation at the Si (111) surface in the temperature range of 900–1180°C.

2. EXPERIMENTAL

The studies were conducted using the original technique of in situ ultrahigh-vacuum reflection electron microscopy (UHV REM), whose possibilities allow visualization of the surface morphology of crystals during sublimation, homoepitaxial and heteroepitaxial growth, the deposition of metals, and interaction with gases in a wide region of substrate temperatures [8]. Using optical lithography and plasma chemical etching, we fabricated square-shaped pedes-

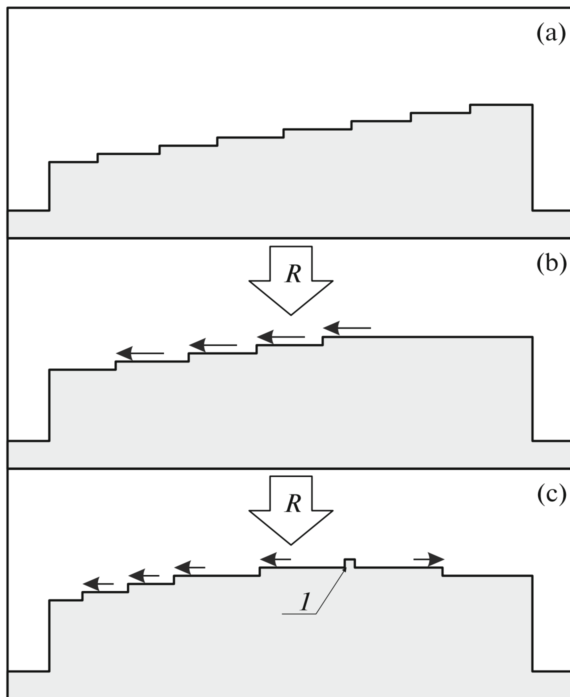

Fig. 1. Schematic representation of the surface morphology (a) after high-temperature annealing and (b, c) during the deposition of silicon. *1* indicates a nucleated 2D island. *R* denotes the silicon flux onto the surface.

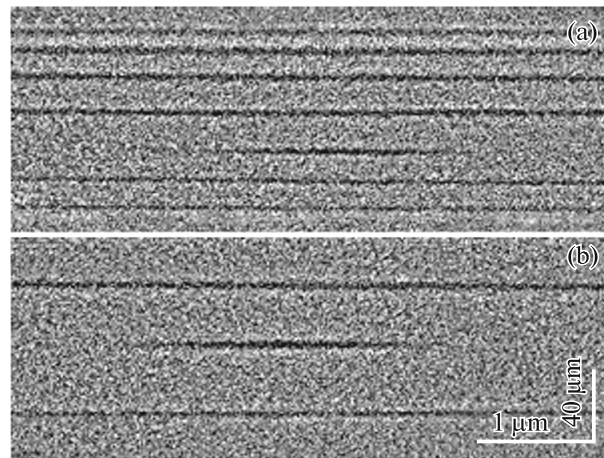

Fig. 2. REM images of the pedestal surface including concentric atomic steps and a nucleated 2D island at a temperature of 1100°C at different silicon fluxes onto the surface: (a) 0.2 and (b) 0.09 ML s^{-1}.

tals at the surface of samples 1 × 8 × 0.3 mm in dimensions. The pedestals were 500 × 500 µm in lateral dimensions and 2 µm in height. After purification of the surface with isopropyl alcohol in an ultrasonic bath and subsequent chemical treatment in petroleum ether, the samples were placed into a UHV REM chamber, in which they were annealed at a temperature of 1300°C with the purpose of removing the natural oxide layer and contaminant particles from the surface. Heating of the sample was conducted by passing an ac current through the sample. A sufficient degree of purification of the surface was indicated by the disappearance of additional reflections related to contaminant particles from the microdiffraction pattern as well as by the reversible (1 × 1) ↔ (7 × 7) superstructure phase transition which is observed at the atomically pure surface of Si (111) at 830°C [9]. The lack of deceleration centers for atomic steps upon displacement during sublimation was also indicative of the high degree of cleaning of the surface from contaminants.

After high-temperature annealing, a system of regular steps was formed on the pedestal surfaces. The spacing between the steps was defined by the angle of deviation of the whole wafer from the crystallographic face (Fig. 1a). Then we deposited silicon onto the sample surface at a temperature of 1000°C. During the deposition process, the steps were displaced towards the lower terraces. As a result of step displacement, a wide terrace up to 200 µm in diameter was formed on the pedestal surface (Fig. 2b). As the terrace size reached the critical value upon the deposition of silicon, a 2D island was nucleated on the terrace (Fig. 2c); then the island grew, thus forming of a new terrace.

Changes in the surface morphology were recorded with a CCD camera (TVIPS FastScan-F114) with a frequency of 25 frames per second. Then we processed the video files, measured the critical terrace diameter at the instant of island nucleation, and determined the nucleation frequency. To reduce the measurement error, we recorded no less than 20 events of 2D island nucleation in each REM video recording of the image.

3. RESULTS AND DISCUSSION

Figures 2a and 2b show typical REM images that illustrate the surface morphology of the silicon pedestal with wide terraces spaced by concentric steps (dark contrast lines) at different silicon fluxes onto the surface. The thin dark contrast line in the central terrace is the image of a nucleated 2D island. Because of the specific features of the formation of electron microscopy images in the REM technique, the round 2D island looks like a highly compressed ellipse [8]. The critical terrace size, at which the new island was nucleated upon the deposition of silicon at a rate of 0.2 ML s^{-1} (Fig. 2a) is smaller than the terrace size at a deposition rate of 0.09 ML s^{-1} (Fig. 2b). This result is consistent with the classical idea of a decrease in the critical terrace size with increasing flux of the material to be deposited onto the surface [10, 11].

We measured the critical terrace size D_{crit} as a function of the frequency of 2D island nucleation on the

central terrace ν, $D_{crit}(\nu)$, at different sample temperatures (900–1180°C). Figure 3a shows the double logarithmic plots of the dependence of the critical terrace diameter squared on the island-nucleation frequency at different substrate temperatures. With high precision, the experimental dependences can be approximated with a power function, with the exponent χ which remains unchanged and corresponds to 0.9 ± 0.05 in the entire temperature range under study. The temperature variation in the coefficient *A* of the power function is shown in Arrhenius coordinates in Fig. 3b. From this dependence, we determined the nucleation activation energy $E_{2D} = 1.5 \pm 0.1$ eV.

The classical theoretical description of the nucleation processes [10, 11] is based on the assumption that, at the surface, there exists a steady-state concentration of unstable nuclei consisting of different numbers of atoms *i* smaller than the critical number *i**. As the critical number *i** is reached, the nucleus becomes stable and only grows in size. To describe the experimental data, we make use of the theory developed on the basis of a classical concept and reported in [12]. In [12], the process of nucleation of a single island on a terrace between steps is considered. The dependence of the critical spacing between steps D_{crit} on the flux of the material onto the surface is

$$D_{crit}^2 = A\left(\frac{R}{\nu_0}\right)^{-\chi}. \quad (1)$$

Here, D_{crit} is the critical terrace diameter, *R* is the silicon flux onto the surface (in ML s^{-1}), ν_0 is the atomic vibration frequency in the crystal, *A* is the coefficient of the power function (the coefficient *A* depends on the effective energy of 2D island nucleation E_{2D}, and χ is the exponent dependent on the critical nucleus size *i**. In the case under consideration, the atomic flux onto the surface *R* can be replaced with the island nucleation frequency ν which corresponds to the flux of the material onto the surface with consideration for the sublimation process. Two limiting cases of nucleation processes are commonly considered. These are (i) the diffusion-limited (DL) process that is limited by the diffusion of adatoms over the surface,

$$\chi = \frac{i^*}{i^*+2}, \quad E_{2D} = \frac{E_i + i^* E_D}{i^*+2}, \quad (2)$$

and (ii) the attachment–detachment-limited (ADL) process that is limited by the interaction of an adatom with a step,

$$\chi = \frac{2i^*}{i^*+3}, \quad E_{2D} = \frac{2[E_i + i^* E_D + (i^*+1)E_{AD}]}{i^*+3}. \quad (3)$$

Here, E_i is the energy of the dissociation of the critical *i**-sized nucleus, E_D is the energy of diffusion of adatoms over the terrace, and E_{AD} is the energy of interaction of an adatom with a step.

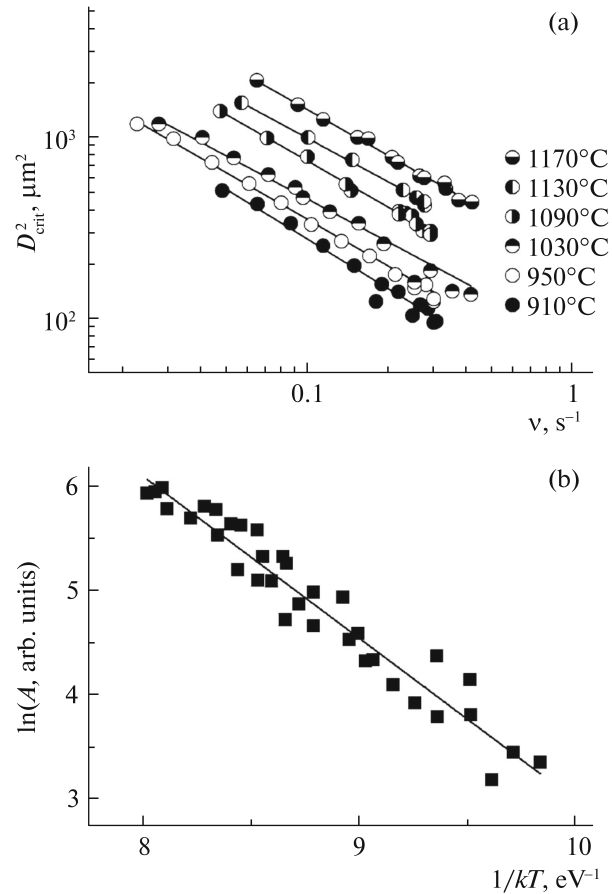

Fig. 3. (a) Double logarithmic plot of the dependence of the critical terrace size squared on the island nucleation frequency at different temperatures (indicated). (b) Semilogarithmic plot of the temperature dependence of the coefficient of the power function *A*.

If it is assumed that mass transfer at the surface occurs via the ADL process, the theoretical values of χ closest to the experimental values obtained in this study are 0.8 and 1. The values 0.8 and 1 correspond to the critical nuclei consisting of two and three atoms, respectively. Taking into account the precision in determining the experimental value of χ = 0.9 ± 0.05, we think that the ADL mode of mass transfer on the silicon surface is improbable. Moreover, in [13–15], it was shown that, at temperatures of 900–1000°C, the DL mode of mass transfer on the Si (111) surface is more probable. Thus, according to formula (2), the experimentally determined value of χ = 0.9 ± 0.05 corresponds to a larger critical-nucleus size. With consideration for the measurement error, we conclude that this size is in the range between 12 and 38 atoms. The critical nucleus size estimated here is somewhat larger than *i** = 9 obtained for the temperatures 850–1100°C in [16].

It should be noted that, at the above critical nucleus sizes, a change in the nucleus size by one atom does not yield a sharp change in the relation between

the fluxes of atoms attached to and detached from the nucleus. Therefore, the limit of the critical nucleus size is blurred, resulting in the existence of a range of nucleus sizes i^*, at which the probability of the formation of a stable 2D island is high. Such a large critical nucleus (12–38 atoms) is actually a 2D island, and the energy of incorporation of an atom into a step is bound to be close to the energy of attachment of the atom to a nucleus. The last-mentioned energy can be estimated as the specific energy of the formation of the critical nucleus E_i/i^*. Using formula (3) and E_D = 1.3 eV [14], we find that the specific energy of formation of the critical nucleus is $E_i/i^* = 0.2 \pm 0.10$ eV. According to the data reported in [14], the specific energy obtained above is close to the energy of the interaction of an adatom with a step of 0.23 eV. This result also suggests that estimation of the critical nucleus size here is adequate.

4. CONCLUSIONS

In this study, we for the first time explore 2D island nucleation at the Si (111) surface during high-temperature epitaxial growth in the temperature range 900–1180°C. It is found that the critical terrace diameter squared is a power function of the frequency of island nucleation on the surface in the entire temperature range under consideration, with the exponent $\chi = 0.9 \pm 0.05$. In this case, the effective 2D-nucleation activation energy is 1.5 ± 0.1 eV. The minimum critical nucleus size is estimated at $i^* = 12$ atoms. The estimated specific energy of formation of the critical nucleus is $E_i/i^* = 0.2 \pm 0.10$ eV. On the basis of the results, it is shown that the kinetics of mass transfer on the Si (111) surface during epitaxial growth in the temperature range 900–1180°C is defined by the diffusion of adatoms over the surface of the crystals.

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