Initial stages of gold adsorption on silicon stepped surface at elevated temperatures

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(Получена 12 сентября 2006 г. Принята к печати 3 октября 2006 г.)

Experimental study performed by ultrahigh vacuum reflection electron microscopy and atomic force microscopy reveals step instability on Si (111) surface during gold deposition at elevated temperatures (higher than 900°C). Our results show that transformations of regular atomic steps into the system of step bunches and *vice versa* depend on the gold coverage and direction of the electrical current heating the sample. The mechanism and conditions of the surface morphology transformations are discussed.

PACS: 61.72.Ji, 68.35.Fx, 68.37.-d

1. Introduction

Understanding of the atomic processes those govern the surface morphology formation during sublimation, homo- and heteroepitaxial growth and foreign atom adsorption is of great interest for surface science. In particular atomic step behavior on a vicinal silicon surface has attracted much interest not only for obtaining new fundamental knowledge but also because it has great importance for device processing. A number of previous works [1–3] shows that the direct electrical current using for sample heating lead to the atomic steps redistribution on the silicon surface during sublimation. Under well-known experimental conditions the system of regular atomic steps transforms into the system of step bunches which consist of the number of atomic steps closely situated to each other.

While a lot of efforts are applied to understand many aspects of step bunching on clean silicon surface, less is known about the influence of foreign atom deposition on the atomic steps behavior at elevated temperatures. Experimental investigations [4] show that submonolayer gold adsorption on Si (111) surface with low miscut angle initiates the changing of the atomic steps distribution (regular steps ↔ step bunches). This step instability depends on the heating current direction, and is attributed to the change of an adatom effective charge [5]. Changing of the surface morphology after gold deposition is also observed on the Si (111) surface with high miscut angle [6,7], but with some differences. When the gold coverage increases the critical one, step bunching is observed at silicon surface irrespective of electrical current direction. This step instability is considered due to the changing of atomic steps properties.

Physical origin of the atomic steps redistribution during gold atom deposition is still controversial. In this paper we have investigated atomic steps behavior on the Si (111) surface at the temperature higher than 900°C during gold deposition under the conditions of direct electric current heating. The main attention has been focused on determination of conditions causing step bunching during gold adsorption.

2. Experimental

Silicon surface morphology observations were performed in an ultrahigh vacuum chamber of a reflection electron microscope (UHV-REM) [8]. The sample, $8 \times 1 \times 0.3$ mm in sizes, cut from nominally flat Si (111) wafer was cleaned by high temperature (1260°C) thermal annealing in ultrahigh vacuum during several minutes. After cleaning procedure reflection high energy electron diffraction (RHEED) patterns demonstrated the reversible superstructural phase transition $(7 \times 7) \leftrightarrow (1 \times 1)$, which took place at 830°C. In addition, no any pinning centers for the motion of the atomic steps during sublimation were observed in REM. Specially developed small-size gold evaporator was placed immediately in the face of the sample to provide gold deposition on the silicon surface. It should be pointed out, that recorded REM-images are foreshortened by factor $1/50$ in the direction of the electron beam incidence due to a small angle between surface and electron beam. After evacuation from the sample chamber of the electron microscope, the samples were analyzed by means of atomic force microscopy (AFM) under ambient conditions.

3. Results and discussion

Fig. 1, *a* represents a typical REM image of the clean vicinal silicon (111) surface at 900°C after high-temperature thermal annealing in the ultrahigh vacuum chamber of the electron microscope. Thin dark wavy lines are atomic steps (0.31 nm in height) on Si (111) surface. The atomic steps moved from the bottom-left to the top-right corner of the image due to evaporation of the silicon atoms during sublimation. The direction of the atomic steps motion

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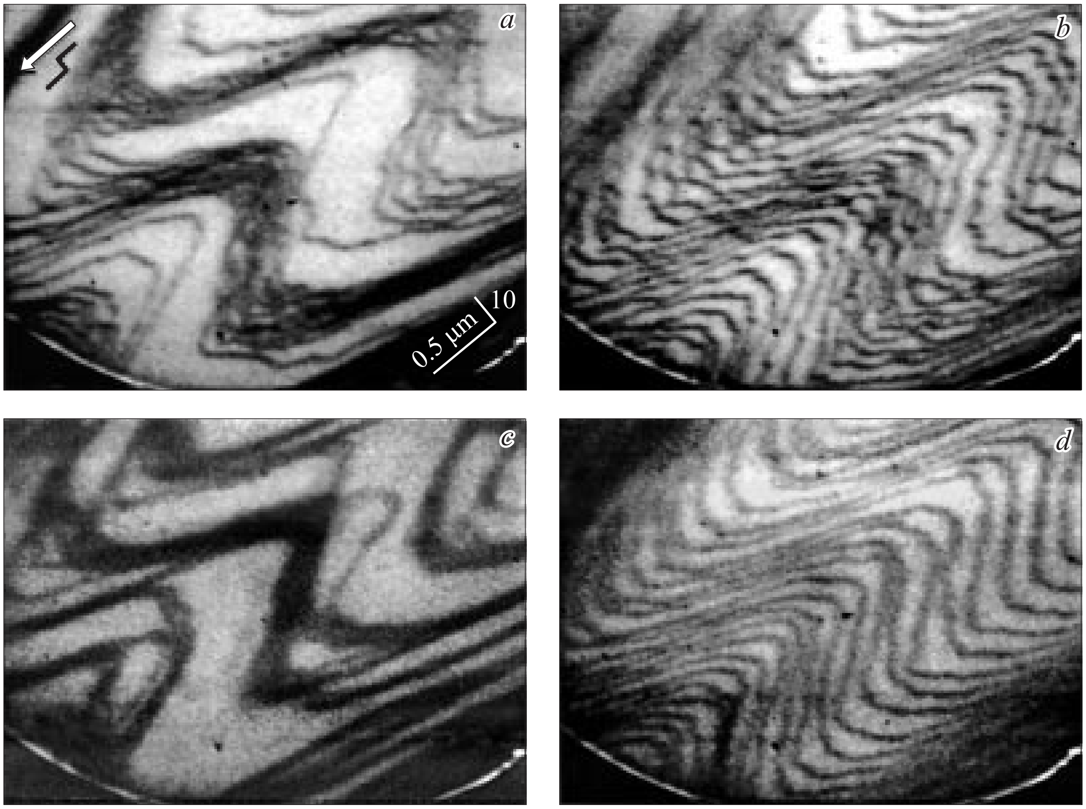

Figure 1. A series of REM-images showing silicon (111) surface morphology transformations at 900°C heated by direct current in the step-down directions during gold deposition. Initially clean silicon surfaces with step bunches (*a*) and after deposition 0.1 (*b*), 0.24 (*c*) and 0.42 ML (*d*) of gold.

during sublimation indicates that terraces in the top-right part of Fig.1, *a* are higher than the ones situated in the bottom-left part of the image.

White arrow indicates the direction of the heating electrical current passing through the crystal. According to previous studies at 900°C the instability of the diffusion linked atomic steps on the clean silicon surface leads to the formation of the step bunches [1]. Step bunches, consisting of a number of closely distributed atomic steps, are clearly identified in Fig. 1, *a* as wide wavy bands of dark contrast. For the step-up direction of the heating current, regular distribution of the atomic steps forms on silicon surface at this temperature. We observed the redistribution of the atomic steps from regular system to the system of step bunches and *vice versa* after switching the electrical current direction in several minutes. Increasing the sample temperature caused increase of atomic steps mobility and redistribution of the atomic steps occurred faster.

When a small amount of gold, less than 0.1 monolayer (ML), was deposited at silicon surface, we observed the first transition of surface morphology. Step bunches dissolved into the regular distributed atomic steps (Fig. 1, *b*) for step-down current direction in agreement with Ref. [4,5]. Silicon sublimation at these temperatures produced slow motion of atomic steps in the step-up direction. Regular distribution of the atomic steps, associated with the first transition of surface morphology (Fig. 1, *b*), was observed at gold coverage below 0.24 ML. Increasing of gold coverage above 0.24 ML caused the second transition of the silicon surface morphology in a way of gold induced step bunches formation (Fig. 1, *c*). Step bunches on silicon surface, formed by gold deposition, were stable in the range of gold coverage $0.24-0.42$ ML. The process of step bunching at this gold coverage occurred faster than at clean silicon surface. At the same time we observed the atomic steps motion in the direction of the lower situated terraces during gold deposition. Further increasing of gold coverage caused regular steps formation as it is shown in Fig. 1, *d*. When the gold amount on the silicon surface exceeded approximately 0.6 ML the formation of three-dimensional islands on the surface (not shown in Fig. 1), probably consisting of mix of gold and silicon atoms was observed. Some of the moving islands were pinned at the step bunches position that is in agreement with Ref. [9]. Recent investigations of the silicon (111) surface morphology transformations after submonolayer gold deposition during thermal annealing at 900°C [10] showed redistribution of the atomic steps at the surface during gold coverage reducing. In the present work gold atoms dissolving and evaporation are almost compensated by careful alignment of gold deposition rate.

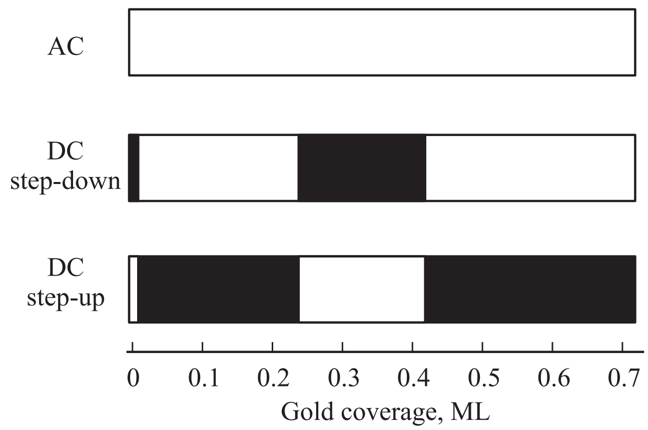

Figure 2. Schematic representation of the silicon surface morphology at 900°C during gold deposition. Dark areas correspond to the step bunched morphology; white areas correspond to the regular distributed steps.

We also investigated the silicon surface morphology transformations during gold deposition when the heating electrical current flows in the step-up direction. After switching the current direction, the system of regular distributed atomic steps (Fig. 1, *b* and *c*) was transformed to the system of step bunches while step bunches (Fig. 1, *d*) were redistributed into regular steps. Heating the sample by passing alternative electrical current was found to produce regular distributed steps throughout the investigated range of gold coverage (0−0.71 ML).

Gold deposition rate was calculated by measuring the time necessary for 5×2 patterns formation on silicon surface at 500°C. During superstructural phase transition $7 \times 7 \rightarrow 5 \times 2$ the silicon surface was visualized in REM. The amount of gold when the whole surface was covered by 5×2 domains was calculated from Au−Si surface phase diagrams [11,12]. After determination of deposition rate, a certain amount of gold atoms was deposited at the silicon surface at 500°C. Then the sample temperature was increased to 900°C and the silicon morphology transformations were observed. From these measurements the critical coverages for morphological transformations were measured as 0.008, 0.24 and 0.42 ML. Fig. 2 represents schematic illustration of the surface morphology transformations at 900°C for alternative (AC) and direct (DC) electrical current heating. Dark and white areas indicate the step bunches and regular distributed atomic steps correspondingly.

It should be pointed out, that some steps on the gold deposited surface moved in the direction of lower situated terraces. This corresponds to the capturing of adatoms by the step, which is usually observed in the homoepitaxial growth. Considering that attached atoms are silicon ones, we suggest the increasing of silicon adatoms concentration on the surface during gold deposition. To verify this assumption we have investigated silicon surface morphology after gold deposition at 900°C and subsequent quenching the sample to room temperature.

In order to reduce the influence of the atomic steps (which are known as perfect surface sinks for adatoms and vacancies) on the diffusion processes on the terraces we have created large step-free areas on the silicon surface. Wide terraces were fabricated with the help of step bunching phenomenon during high temperature annealing of the sample in the ultrahigh vacuum chamber of the reflection electron microscope. Fig. 3 shows typical 5000×5000 nm images of the silicon (111) surface before (*a*) and after (*b*) gold deposition and quenching the sample to room temperature, obtained by means of atomic force microscopy. Atomic steps of 0.31 nm in height are shown in the images (Fig. 3, *a*) as thin lines dividing terraces on the surface. Fig. 3, *b* represents the silicon surface after deposition of 0.2 ML of gold. One can see the additional bright spots on the terraces between the atomic steps which correspond to the high density of small islands. Contrast of the islands coincides to the contrast of higher situated

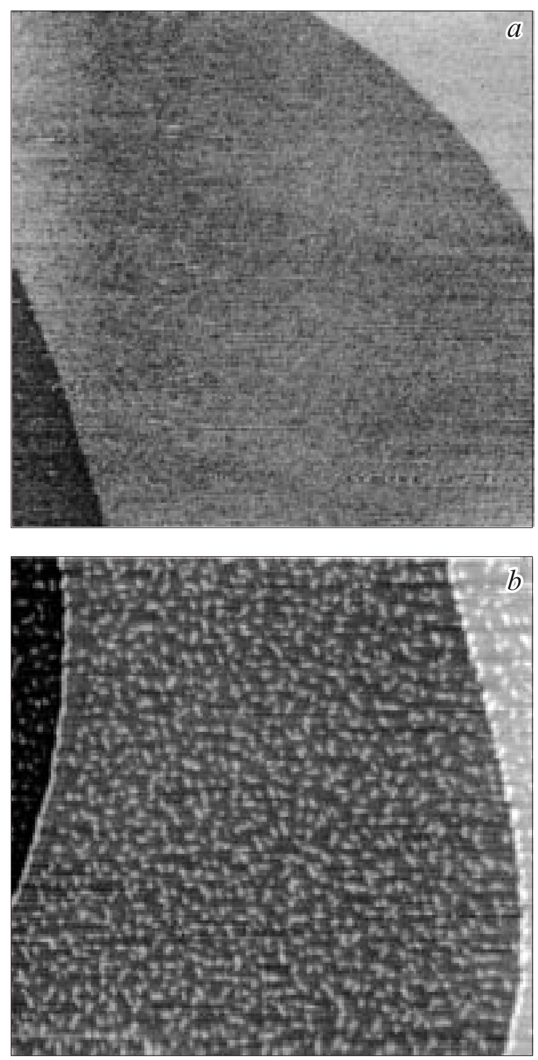

Figure 3. Typical 5000×5000 nm AFM-images of clean silicon (111) surface after quenching with step-free terraces and atomic steps (*a*) and with two-dimensional islands, induced by gold adsorption (*b*).

terrace. Precise AFM measurements showed that the height of the islands corresponds to a monoatomic step on the silicon surface. The density and the average size of the islands depended on the temperature which the substrate was quenched from, cooling rate, and gold coverage.

The formation of two-dimensional islands on the terraces gives the evidence of the increased adatom concentration on the surface, which can be obtained by the diffusion of silicon atoms (self interstitials) from the bulk to the surface. This is in consistent with the fact, that diffusion of gold in the silicon bulk proceeds *via* kick-out reactions between interstitial gold and silicon lattice sites [13], that may result in formation of substitutional gold and silicon self interstitials. Out-diffusion of silicon self interstitials to the surface may cause the increasing of the adatom concentration.

Let us consider the possible mechanism for silicon surface morphology transformations on the gold deposited surface at elevated temperatures. Diffusion of the silicon adatoms on atomically clean silicon surface may be affected by the applied electrical field [14,15]. Typically this effect attributed to the electromigration of charged silicon adatoms under applied electric field. Electrical current induces drift of adatoms which leads to the appearance of the asymmetrical distribution of the adatom density on the traces between atomic steps. Changing the polarity of applied electrical field or the sign of the effective charge may modify the correlation between adatom fluxes from the steps to lower and upper situated terraces (attachment/detachment rates) which can induce the instability of the diffusion linked train of atomic steps [16–18].

When a small amount (above the first critical concentration) of gold is deposited on the surface, effective charge of silicon adatoms changed to the opposite one as it was described in [4], due to interaction with negative charged gold adatoms on silicon surface. As a result of changing the effective charge of silicon atoms, the redistribution of the atomic steps occurs (Fig. 1, *b*). When the amount of gold exceeds the second critical concentration, the penetration of gold atoms into the silicon bulk became significant. The incorporation of gold atoms into the subsurface area results in increased concentration of silicon adatoms and change of surface properties. This is confirmed by the observations of atomic steps motion in the direction of the lower situated terraces at this conditions and formation of islands after quenching the sample. On the one hand, increasing of the silicon adatoms on the terraces may results in reversible changing of the effective charge of silicon adatoms to the positive one. On the other hand, the diffusion length of the silicon atoms on the gold deposited surface may be increased. It should be pointed out, that increase of the silicon diffusion length on $Si(111)$-$(5\times 2)-Au$ surface reconstruction was observed at lower temperatures [19]. Both effects may result in the second transformation of the surface morphology (Fig. 1, *c*).

The diffusion of gold atoms into the silicon bulk is determined by the sample temperature and gold surface concentration. Increasing of the gold concentration on the silicon surface caused accumulation of gold atoms on the surface due to finite rate of dissolving of gold atoms into the silicon. As a result, number of negative charged gold adatoms on the terraces increases, and the effective charge of silicon atoms changes again to the opposite one (in a way similar to the first transition). This can explain the third transition of the surface morphology (Fig. 1, *d*).

Step bunches on the silicon surface may be considered as the areas with high density of the atomic steps which are usually observed at surfaces with high miscut angle. Our observations of the step bunches during gold deposition reveal the same behavior as for rare distributed atomic steps. The interstep distance inside the bunch reduced or increased depending on the gold coverage. Taking this into account and the fact that according to our results the step bunching observes for step-up current direction when the gold coverage is above 0.42 ML and for step-down direction when the gold coverage is inside the range $0.24-0.42$ ML, we conclude that independence of the step bunching on the heating current direction observed in [6] is due to inaccurate gold coverage measurements. Our investigations also show decreasing of atomic step fluctuations in the last gold coverage range (above 0.42 ML) for step-down current direction which caused straightening of the atomic steps (Fig. 1, *d*).

4. Conclusion

In the present paper, reversible transformations of the regular system of atomic steps into the system of step bunches on Si (111) surface induced by gold adsorption is investigated and mechanism of the atomic steps rearrangement is discussed. In contrast to current induced step bunching at clean surface, gold induced step bunching takes place at constant temperature and depends on the gold coverage. Four ranges of gold coverage and three transitions of the surface morphology (from regular steps to step bunches and *vice versa*) are found. The critical concentrations corresponding to each transition are estimated.

This work has been partly supported by RFBR (04-02-16693) and by the programs of Ministry of Education and Science of Russian Federation.

References

[1] A.V. Latyshev, A.L. Aseev, A.B. Krasilnikov, S.I. Stenin. Surf. Sci., **213**, 157 (1989).
[2] Y. Homma, R.J. McClelland, H. Hibino. Jap. J. Appl. Phys., **29**, L2254 (1990).
[3] Y.-N. Yang, E.S. Fu, E.D. Williams. Surf. Sci., **356**, 101 (1996).
[4] A.V. Latyshev, H. Minoda, Y. Tanishiro, K. Yagi. Surf. Sci., **401**, 22 (1998).
[5] A.V. Latyshev, H. Minoda, Y. Tanishiro, K. Yagi. Appl. Surf. Sci., **130-132**, 60 (1998).
[6] H. Minoda. Phys. Rev. B, **64**, 233 305 (2001).

[7] H. Minoda. Thin Sol. Films, **424**, 40 (2003).
[8] A.V. Latyshev, A.B. Krasilnikov, A.L. Aseev. Microsc. Res. Technique, **20**, 341 (1992).
[9] A.V. Latyshev, D.A. Nasimov, V.N. Savenko, A.L. Aseev. Thin Sol. Films, **367**, 142 (2000).
[10] S.S. Kosolobov, S.A. Song, L.I. Fedina, A.K. Gutakovskij, A.V. Latyshev. Pis'ma v Zhurnal Éksperimental'noy i Teoreticheskoy Fiziki, **81** (3), 149 (2005). [JETP Lett., **81** (3), 117 (2005)].
[11] D. Grozea, E. Bengu, L.D. Marks. Surf. Sci., **461**, 23 (2000).
[12] S. Ino. MSA Bulletin, **23**, 1109 (1993).
[13] U. Gosele, W. Frank, A. Seeger. Appl. Phys., **23**, 361 (1980).
[14] S. Stoyanov. Jap. J. Appl. Phys., **29**, L659 (1990).
[15] S. Stoyanov. Jap. J. Appl. Phys., **30**, 1 (1990).
[16] D. Kandel, J.D. Weeks. Phys. Rev. Lett., **74**, 3632 (1995).
[17] H. Dobbs, J. Krug. J. Phys. I France, **6**, 413 (1996).
[18] S. Stoyanov. Surf. Sci., **370**, 345 (1997).
[19] M. Copel, M.C. Reuter, E. Kaxiras, R.M. Tromp. Phys. Rev. Lett., **63**, 632 (1989).

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