Atomic Steps on the Si(111) Surface during Submonolayer Gold Adsorption

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Abstract—The effect of adsorption of submonolayer gold coatings on the Si(111) surface morphology in the temperature range 850–1260°C has been investigated by means in situ ultrahigh-vacuum reflection electron microscopy and ex situ atomic force microscopy. Reversible transformations of the silicon surface: from regular monoatomic steps to step bunches, depending on the gold coverage and direction of the electric current resistively heating the crystal, have been revealed. Stability of the regular distribution of monoatomic steps upon heating of the crystal by an alternating current is shown. The effect of an electric field applied to the sample on the diffusion of silicon and gold adatoms has been analyzed taking into account the effective adatom charge.

INTRODUCTION

Development of modern solid-state physics during the last years is based on the fabrication and investigation of new objects and materials, among which semiconductor low-dimensional systems—nanostructures—occupy a special place. Such structures are formed, in particular, during submonolayer deposition of metal films [1, 2]. At the same time, adsorption of impurity atoms plays an important role in the structural processes occurring on crystal surfaces. Let us consider some regularities of impurity adsorption on a semiconductor surface by the example of the best studied metal–semiconductor system: gold on the Si(111) surface. Deposition of 0.48 monolayers (MS) of gold leads to the (5 × 2) surface reconstruction at 500°C, which is clearly observed in diffraction patterns [3]. The physical reasons for the unit-cell transformation are generally related to the relaxation processes, which tend to minimize the surface energy. It should be noted that a change in the direction of electric current heating the crystal does not affect the distribution of atomic steps during surface transformation. Polycrystalline nucleation and growth of superstructural (5 × 2) domains leads to a change in the distribution of atomic steps due to the formation of step clusters (bunches) at the boundaries of growing domains [4]. At large coverage and/or lower substrate temperatures, three-dimensional gold islands are formed according to the Volmer–Weber theory [5]. The density and sizes of three-dimensional islands, as well as their chemical composition, depend strongly on the substrate temperature [3]. In accordance with the phase diagrams [6, 7] and experimental data [5, 8], superstructural transformations initiated by gold atoms are not observed on the Si surface at temperatures above 830°C. The above-mentioned regularities of gold adsorption on the silicon surface indicate that it is necessary to establish the contribution of adsorbed gold atoms to the structural processes occurring on the surface at temperatures excluding the surface transformation, i.e., above 830°C. The purpose of this study is to analyze the effect of adsorbed gold on the substrate surface morphology at high temperatures.

EXPERIMENTAL

The surface relief was analyzed by in situ ultrahigh-vacuum reflection electron microscopy (UHV REM) [9]. A silicon sample 10 × 1 × 0.3 mm³ in size was cut from a standard silicon wafer. The misorientation angle between the normal to the surface and the [111] direction was less than 1°. After degreasing the sample surface in toluene, the sample was fixed in a holder with annealed tantalum contacts, which made it possible to pass electric current through the sample. Further cleaning of silicon surface was performed in the UHV chamber of an electron microscope via thermal annealing at 1300°C for 10 min to remove the native oxide layer and contaminating particles from the crystal surface. The atomically clean state of the silicon surface was evidenced by the absence of hindering centers for atomic steps at their motion during sublimation at elevated temperatures. The diffraction pattern obtained at temperatures above 830°C does not contain additional reflections due to particles of silicon carbide or other contaminations. With a decrease in the crystal temperature, we detected the reversible superstructural (1 × 1) $\rightarrow$ (7 × 7) phase transition, which is observed on the atomically clean Si(111) surface at a temperature of 830°C.
Gold was deposited from a tungsten crucible by resistive heating of a tungsten wire contacting with a gold foil. The gold deposition rate was calibrated from the phase diagrams of the superstructural transformations initiated by gold deposition on the Si(111) surface at low temperatures \[6, 7\]. The occupancy of the silicon surface with superstructural domains was determined directly by visualization of domains in REM images. After extraction of the samples from the electron microscope chamber, the silicon surface with deposited gold was analyzed on a SOLVER P-47H atomic force microscope (NT-MDT).

**RESULTS AND DISCUSSION**

Figure 1a shows an REM image of the Si(111) surface with steps after UHV thermal annealing at a temperature of 1260°C. The thin dark lines intersecting the figure in the vertical direction are images of atomic steps, whose height is 0.31 nm. At temperatures exceeding the point of the superstructural phase transition \((1 \times 1) \rightarrow (7 \times 7) (830°C)\), the REM images indicate motion of atomic steps (initiated by sublimation processes) toward upper terraces. The directed motion of steps is due to the successive detachment of atoms from the step edge, their diffusion along the terrace, and desorption from the terrace into vacuum. The velocity of monoatomic steps is described by the classical Burton–Cabrera–Franck theory \[10\] for the motion of a series of parallel atomic steps during growth and sublimation. However, the motion of steps over the crystal surface during sublimation is not always uniform. Asymmetry of adatom diffusion fluxes from a step to the adjacent terraces may lead to instability of the atomic step motion \[11\]. An example of the occurrence of an instability of such kind is the formation of atomic step bunches \[12\]. In this case, the asymmetry of diffusion fluxes is induced by an applied electric field, which acts on the adatoms having an effective charge \[13\]. Figure 1b shows an REM image of the Si(111) surface after heating the crystal at 900°C by passing an electric current through it in the direction to lower terraces. One can see aggregation of atomic steps into groups of several steps; this aggregation is the initial stage of the formation of atomic step bunches. As a result of step aggregation, terraces are formed in the regions between bunches, which exceed several times the sizes of the initial terraces (Fig. 1a). A change in the polarity of the voltage applied to the sample led to reversible transformation of the system of step bunches into a system of regularly located monoatomic steps.

To study the effect of gold adsorption on the surface morphology transformation at elevated temperatures, we performed experiments on deposition of submonolayer gold coatings on the silicon surface containing a set of regular steps (Fig. 1a) and a set of step bunches (Fig. 1b). In these experiments, we took into account the change in the concentration of gold atoms on the silicon surface due to the processes of gold sublimation and dissolution in the bulk of the crystal. To measure the amount of gold on the crystal surface at a temperature of 900°C, we performed experiments on high-temperature deposition of gold with subsequent rapid cooling (quenching) of the sample to room temperature after switching off the source of gold. A high cooling rate (about 400°C s\(^{-1}\)) was obtained due to the additional cooling of the sample holder with liquid nitrogen. After cooling the sample to room temperature, we analyzed the reflection high-energy electron diffraction micropatterns of the crystal surface. This analysis revealed the presence of additional superstructural reflections corresponding to the superstructural transformation of the Si(111)-(5 × 2)-Au type, initiated by gold atoms. Analysis of the REM images obtained in fractional reflections made it possible to measure the