Phase transitions on clean (320) silicon surfaces

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The phase transitions between the structures Si (320)–$1\times 2^{810\,^\circ\mathrm{C}}\leftrightarrow$ facets $\{23\ 15\ 3\}^{880\,^\circ\mathrm{C}}\leftrightarrow$ Si (320) -1×1, occurring in a thin surface layer on a clean silicon (320) surface with changing temperature are investigated by the slow-electron diffraction method. The kinetics of the structural changes at various temperatures is investigated by measuring the time dependence of the reflection intensities. It is concluded that the observed phase transitions are of first order.

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1. INTRODUCTION

Reversible structure transitions of the order-order type are observed in the surface layers of clean silicon and germanium surfaces when the temperature is changed.[1-4] These transitions are observed on surfaces with definite orientations.[5] In the present study, using the method of low-energy electron diffraction (LEED), we have investigated the structure transition on a silicon (320) surface cleaned in ultrahigh vacuum. This transition manifests itself in that the surface constituting the (320) cystallographic plane becomes reversibly restructured in a definite temperature range into a set of planar facets. We determine here the indices of the facet planes and investigate the kinetics of the restructuring during the phase transition.

2. PROCEDURE

We used for the investigations *p*-silicon samples with resistivity 5–10 Ω·cm and with dimensions 16×5×0.8 mm. The surfaces with the required orientations were obtained by cutting an ingot oriented by the x-ray method. The orientation accuracy was approximately 1°. To remove the layer spoiled by the grinding and polishing, the sample surfaces were oxidized to a depth of the order of 1 μm, and prior to installation into the vacuum chamber of the LEED apparatus the oxide was removed by dissolution in hydrofluoric-acid vapor. The samples were secured in the chamber with tantalum conducting clips which served to heat the samples with direct or alternating current. Tungsten-wire probes were used to determine the temperature by measuring the resistance of the samples. The clean surfaces were obtained by heating the sample in ultrahigh vacuum at temperatures above 1200 °C.

To observe the LEED patterns from the surface at increased temperatures, the samples were heated with direct current, so as not to distort the diffraction patterns. The reflection intensities were measured with a spot photometer.

3. STRUCTURAL TRANSITIONS ON A CLEAN Si (320) SURFACE

It follows from the LEED data that when the temperature of a clean (320) silicon surface is varied, a definite sequence of reversible structural transitions take place (Fig. 1). At low temperatures one observes from the sample surface diffraction patterns (Fig. 1a) that contain, in addition to reflections of integer order from the (320) plane, which constitute the $[\bar{2}30]$ and $[2\ 3\ 13]$ series, also reflections of fractional orders, which form $[\bar{2}30]$ series located halfway between the corresponding series of integer reflections (see the scheme in Fig. 2). The distances between the reflections of fractional order in the $[\bar{2}30]$ series are half the distance between the reflections of integer order in the corresponding direction. These patterns can be interpreted as superpositions of the patterns from domains of two types (Fig. 3), the formation of which is due to the fact that two equivalent directions $[\bar{2}31]$ and $[2\bar{3}1]$ are present on the (320) surface. Each of the domains is characterized by a surface structure Si(320)–1×2. The period in the unit cell of the surface structure in the (320) plane is doubled along the $[001]$ direction.

Raising the temperature restructures the surface. The result are LEED patterns (Fig. 1b) that indicate that the surface is made up of facet planes whose diffraction reflections move relative to the positions of the reflections from the (320) plane when the energy of the primary electrons changes. The LEED pictures contain two equivalent systems of reflections moving counter to each other when the energy of the primary electrons changes. This points to the presence of two groups of facet planes. Figure 2 shows one system of such reflections.

A faceted surface exists in a definite temperature range, outside of which it is again restructured into a surface corresponding to the atomic plane (320). At high sample temperatures the LEED patterns contain

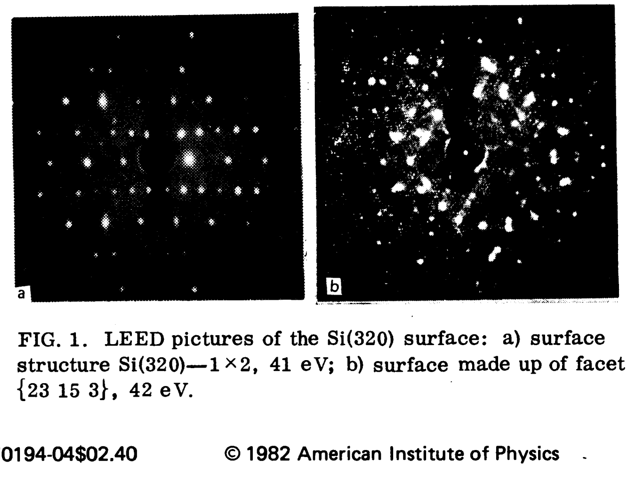

FIG. 1. LEED pictures of the Si(320) surface: a) surface structure Si(320)—1×2, 41 eV; b) surface made up of facets {23 15 3}, 42 eV.

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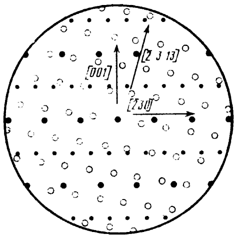

FIG. 2. LEED patterns of the Si(320)—1×2 and of the facet plane (23 15 3): large black circles—reflexes of integer order from the (320) plane; small dark circles–reflections of half-integer order from the (320) plane; light circles–reflections from the facet plane (23 15 3).

only reflections of integer order and no reflections with orders that are multiples of $\frac{1}{2}$. The vanishing of the fractional-order reflections with increasing temperature is observed in LEED from most investigated silicon surfaces (see Ref. 5). It is connected with transitions of the order-disorder type in the surface structure. The structure-change sequence itself on the Si(320) surface is the following: flat surface–faceted surface–flat surface. It is similar to the previously described[6] sequence of transitions on a clean Ge(110) surface. The temperatures at which one surface structure changes into another are well reproducible on one and the same surface, but the temperature straggling for surfaces of different samples reached 15% of the absolute temperature. This is due to the strong dependence of the transition temperature on the orientation accuracy and surface-finish quality. The results that follow pertain to a sample on whose surface the transition temperatures were 810 and 880 °C.

To obtain the Miller indices of the facet plane it is necessary to determine at least two directions lying in this plane. One of the directions can be identified by determining the direction of motion of the reflections from the facets relative to the reflections from the (320) plane. It turned out to be close to [001], from which it follows that the direction of the line of intersection of the sought plane with the (320) plane is close to [$\bar{2}$30], and the period in this direction, as follows from the LEED pictures, should amount to $\frac{3}{2}$ of the period in the same direction in the atomic (320) plane. In the latter plane this direction is [691].

To obtain the second direction lying in the plane of the facet, one determines the projections of any particular period on the [320] direction, perpendicular to the plane, and on the (320) plane. The first quantity was determined from the electron energies at which the reflections from the facets cross in succession the mirror reflection from the (320) plane. It turned out to be equal to double the distance between the (320) atomic planes, i.e., 0.753 Å. It follows therefore that the vectors of the unit cell of the sought plane should be directed from the atom located at the origin and lying in the (320) plane to the atom in another (320) plane located two interplanar distances below the initial one. Using these data, as well as the diffraction pattern from the sought plane, we determine the indices of the two groups of planes, (23 15 3) and (23 15 $\bar{3}$) which are present on the surface and make an angle 6.26° with the (320) plane. The arrangement of the atoms and of the unit cell on the (23 15 3) surface is shown in Fig. 4.

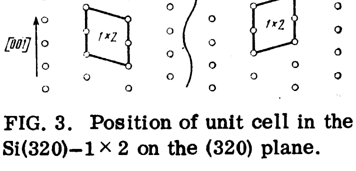

FIG. 3. Position of unit cell in the domains of the structure Si(320)–1×2 on the (320) plane.

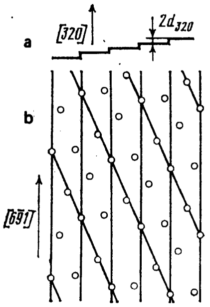

FIG. 4. Scheme of ideal (23 15 3) surface: a—projection of the (23 15 3) plane on the ($\bar{6}\bar{9}\bar{1}$) plane; b—projection of the (23 15 3) plane on the (320) plane. The lines mark the edges of the surface unit cells.

4. KINETICS OF STRUCTURAL TRANSFORMATIONS

The structural transformations on the Si(320) surface, at a fixed temperature, manifest themselves on the LEED picutres in a gradual replacement of one system of reflections by another, thus pointing to a jumplike character of the restructuring of the crystal lattice. The intensities of the reflections are proportional to the area of the surface from which the diffraction is observed. Therefore, by measuring the intensities of the reflections corresponding to one of the phases on the surface, as a function of the time at various temperatures, we can obtain information on the kinetics of the phase transitions. It can be assumed here that the measured intensity is proportional to the fraction of the surface that is being converted.

The time dependence of the intensities of the reflections from the appearing facets {23 15 3} at different temperatures in the range 810–880 °C is shown in Fig. 5. The character of the time dependence of the inten-

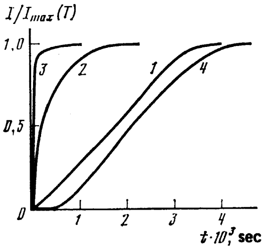

FIG. 5. Intensities of reflections from the (23 15 3) surface as functions of the restructuring time at different temperatures: 1) 814°C, 2) 827°C, 3) 837° C, 4) 877°C.

sity was the same for the different reflections from the facet planes. The plots shown in Fig. 5 pertain to one of the reflections at a primary electron energy 37 eV. The saturation of the curves is evidence of the termination of the restructuring process.

The restructuring at temperatures above 880 °C always took place within a time comparable with the time of establishment of the sample temperature, and the transitions at a temperature below 810 °C required a longer time than the time required to establish the sample temperature when changing the heating current. For this reason, the kinetics of the restructuring of the surface bounded by the facets and the surface containing the surface structure Si(320)–1 × 2 could be investigated only at temperatures below 810 °C. Since the time of restructuring in the latter case could greatly exceed the time of establishment of the sample temperature, it was possible to preserve structure with the facets on the surface by rapidly cooling the sample. The time dependence of the intensities of the reflections at various temperatures in the course of the change to the surface structure Si(320)–1 × 2 were similar to curve 2 on Fig. 5.

Figure 6 shows the temperature dependence of the time of restructuring of the Si(320)–1 × 2 surface into a faceted surface. It can be seen that the time of the restructuring from a smooth surface to a faceted one increases as the transition temperatures are approached, and this is due to the influence of the supercooling on the rate of the phase transition.

Phase transitions usually occur via the onset of centers of a new phase and their subsequent growth; this takes place also on a surface.[7] The kinetics of the phase-transition process is described by the Kolmogorov equation,[8,9] which assumes, for the fraction η of the converting surface, as a function of the time t of the process, the form

$$\eta(t)=1-\exp\left[-\int_0^t \rho(\tau)S(t-\tau)d\tau\right], \qquad (1)$$

where $\rho(\tau)$ is the nucleation rate and $S(t-\tau)$ is the area of the growing center of the new phase.

The nuclei were assumed to be disks that grow with a radial velocity v. Better agreement between the experimental results and those obtained theoretically from Eq. (1) was obtained by assuming in the calculations that the velocity is determined by surface diffusion, i.e., that its dependence takes the form

$$v=\beta(D_s/t)^{1/2},$$

where D_s is the coefficient of diffusion mass transport[10,11] and β is a constant parameter determined by the equilibrium concentration of the adatoms that diffuse towards the boundary of the new phase.

As for the nucleation rate, we consider two cases: a stationary rate ρ_0 of nucleation in a fraction of the unaltered surface, when $\rho(\tau)=\rho_0[1-\eta(\tau)]$, where ρ_0 is a constant, and the case when a constant number N_s of nuclei is produced during the initial stage and remains constant during the growth process. In the former case we have from (1)

$$\eta(t)=1-\exp\left\{-\pi\beta^2D_s\rho_0\int_0^t[1-\eta(\tau)](t-\tau)d\tau\right\}$$

and in the latter

$$\eta(t)=1-\exp(-\pi\beta^2D_sN_st).$$

An analysis of the kinetic curves has shown that formula (2) describes well the experimental relations obtained near the phase-transition points (curves 1 and 4 of Fig. 5). The kinetic curves plotted farther from the phase-transition points (curve 2 of Fig. 5) are described by expression (3). In the latter case the rate of the process is determined by the surface self-diffusion. The slowing down of the process near the phase transition is evidence that the limiting stage here is that of nucleus formation. At temperatures close to the phase-transition point, a delay may be observed in the formation of the new phase during the initial stage (curve 4 of Fig. 5). The metastable state of the surface could be preserved for a long time (~10 min).

At temperatures corresponding to the middle of the temperature interval 810–880 °C, where the restructuring of the surface is faster (curve 3 of Fig. 5), a deviation of the shape of the kinetic curves from that described by formula (3) was observed, as manifest by a slowing down of the process on the last section. This may be caused by coalescence, as a result of strong supersaturation, of the nuclei produced during the initial stage of the growth.

The kinetics of the phase transition of the faceted surface into a flat one is described by formula (3), i.e., it is determined by the process of surface self-diffusion. Using the dependence of the restructuring time on the temperature, as before,[12] we determined the activation energy of this process, which turned out to be 1.6 ± 0.2 eV. This energy pertains to the entire restructuring process, which includes such elementary acts as the detachment of an atom from the point it occupies in the crystal lattice, the diffusion proper, and the inclusion of the adatom in the lattice (if the process follows the atom-diffusion mechanism). The obtained activation energy is much lower than the values known for self-diffusion of silicon in bulk[13,14] and is less than the previously obtained[12] activation energy for the process of restructuring of a surface oriented near the (111) plane and having steps of height equal to one interplanar dis-

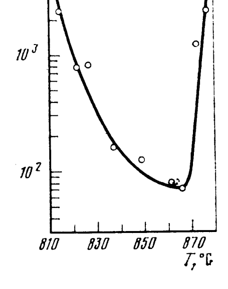

FIG. 6. Temperature dependence of the time of restructuring of the surface with structure Si(320)—1 × 2 into a faceted surface.

tance into a surface with steps two interplanar distances high. The presence of distinct reflections upon diffraction from a surface made up of facets is evidence that the size of each of the facets is not less than the coherence length of the electrons, i.e., it amounts to hundreds of angstroms. It can be assumed that the diffusion length of the atoms upon restructuring of a faceted surface into a surface with the structure Si(320)–1 × 2 amounts to half the distance between them. Assuming by way of estimate of diffusion length 100 Å, we obtain for the coefficient of surface self-diffusion

$$D_s = 2 \cdot 10^{-6} \cdot e^{-1,6/kT}\ \text{см}^2/\text{с}.$$

Thus, according to the LEED data, the transformation of one surface structure into another on a clean Si(320) surface takes place jumpwise. In the course of the transformation, there can exist on the surface simultaneously sections belonging to different phases, and the high temperature phase can be frozen on the surface by a rapid cooling of the sample. An analysis of the restructuring kinetics shows that it agrees well with the kinetics of the phase transition that takes place via formation and growth of nuclei. Thus, the phase transitions of the order-order type on the (320) surface of silicon are of first order. Investigations of the kinetics of the phase transitions yield information on the mass transport over the surface and on surface self-diffusion.

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