

Contribution to the theory of reconstruction of the surface of a semiconducting crystal

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A method based on electrostatic interaction between surface electronic states and the average surface charge and its fluctuations is proposed for the reconstruction of clean faces of semiconducting crystals. The model considered explains the experimentally observed influence of adsorbed atoms on the surface structure, as well as certain metastable properties of the reconstructed surfaces. The possibility of a transition between different superstructures under the influence of laser radiation is predicted, and also a change of the surface in an external electric field.

I. INTRODUCTION

The structures of clean faces of a semiconducting crystal is far from always identical with those of the atomic planes of the same orientation in the bulk of the crystal. For example, various superstructures exist on a number of faces of silicon and germanium single crystals,^{1,2} and the period and symmetry of such superstructures depend on the surface temperature. Thus, the germanium and silicon faces Ge(111) and Si(111) obtained by cleavage in ultrahigh vacuum at room and lower temperatures have a 2×1 superstructure. When a Ge(111) surface is annealed, the half-integer reflections on the LEED pattern, corresponding to the 2×1 superstructure, vanish at $T \approx 300$ K. Above this temperature one observes weak reflections corresponding to Ge(111) – 2×8 surface structure. Their intensity increases and reaches a constant value at $T \approx 300$ K.³

A similar phenomenon is observed on an Si(111) surface: the transition from Si(111) – 2×1 to a new 7×7 superstructure begins at $T \approx 500$ K and is completed fully at $T \approx 650$ K (Ref. 4). There are indications⁵ that at high temperatures ($T \approx 1150$ K) the periodicity 1×1 of the symmetry of the atomic planes in the bulk of the crystal is restored. The crystallography of such superstructures on different faces of various semiconducting crystals turned out to be most diverse. Thus an Si(110) surface cleaved in ultrahigh vacuum at room temperature has a 4×5 superstructure that goes over reversibly into 2×1 when annealed to 870 K. Such a structure, in turn, is found to be unstable to 5×1 reconstruction at 1020 K.⁶ There are many such examples, but the most investigated ones are the (111) faces of germanium and silicon, to which we confine ourselves.

An important properties of the described reconstruction is the presence on such faces of narrow surface electronic states (SES) which are observed near the Fermi level of the crystal. One of the first investigations of the level spectrum on a Ge(111) surface was carried by the method of photoemission and thermionic work functions.⁷ The authors of Ref. 7 analyzed the agreement between the experimental data and various forms of SES distribution and arrived at the conclusion that the most probable is a spectrum model with two SES groups located on the two sides of the Fermi level

and separated by a narrow gap (~ 0.1 eV). The density of the surface electrons contained in these bands was estimated at $N_{\text{sur}} \sim 10^{12} - 10^{13} \text{ cm}^{-2}$. The total charge concentrated in the SES is negative, causing an upward buckling of the bands by ~ 0.3 eV on high-resistance crystals. The results of Ref. 8 fully confirmed the data of Ref. 7 on the photoemission and thermionic work functions and band buckling, as well as the conclusion that a gap exists in the SES spectrum. Recent photoemission-spectroscopy investigations^{9,10} also confirm the data on the SES spectrum on the Ge(111) surface.

Interesting results were obtained in measurements of the photoemission and thermionic work functions following a transition to a Ge(111) – 2×8 structure. It was shown that such a transition decreases the band buckling by 0.12 eV. This conclusion was confirmed by data on the quasisurface conductivity and mobility of the field effect.^{3,11}

Similar results were obtained also for the Si(111) – 2×1 surface. The gap in the SES spectrum was found to be ~ 0.25 eV (Re. 12), and the distance from the Fermi level to the edge of the valence band was $E_F - E_v = 0.33$ eV.¹³ A change to a 7×7 structure alters the surface charge and changes the band buckling: $E_F - E_v = 0.51$ eV.¹⁴

Various models were proposed for the reconstruction of 2×1 faces. In one of the first models^{15,16} was considered the redistribution of the electrons on the surface “broken” bonds as a result of alternating upward and downward replacement of the surface atom rows. In another model^{17,18} it was proposed that the surface atoms follow a zig-zag path over the face surface in such a way that the atoms of each row are π -coupled via their “broken” bonds. It should be noted that at present there is no definite evidence favoring either model. Many known experimental results, however, agree with the π -bond model. Among the refutations of the vertical-displacement model are studies using photoelectronic spectroscopy,^{9,13,19} LEED,²⁰ and ion scattering.²¹ On the other hand, many workers call attention to the disparity between their experimental results and the prediction of the π -bond model.^{10,22} The authors of Ref. 23 state that only allowance for both types of displacement (along the surface and perpendicular to it) can explain incontrovertibly all the results of photoelectronic-spectroscopy, LEED, and other experiments.

Notice must also be taken of one more model,²⁴⁻²⁶ in which it is proposed that doubling the period along one direction on the surface is due to the appearance of an antiferromagnetic spin waves. The experiments of Ref. 27, however, seem to contradict this proposed reconstruction. We note that whereas the 2×1 structures of Si(111) and Ge(111) faces are described by numerous calculations within the framework of the model presented above, there are only various hypotheses for the description of the high-temperature superstructures of the same faces. We wish to call attention, however, to a model²⁸ that describes the appearance of the 7×7 structure on the Si(111) face. This model takes into account the band character of the surface electronic states, and attributes the reconstruction of the face to the onset of a charge density wave in the system of surface atoms.

In contrast to models proposed for the description of the 2×1 structure, which are of variational character, in Ref. 28 it is proposed to attribute the onset of the charge density wave to a definite mechanism connected with Peierls instability in the system of surface atoms.

Let us dwell now on the shortcomings possessed, in our opinion, by the models listed above. First, as already noted, most are only variational, i.e., definite displacements are introduced into the system of surface atoms, the total system energy is next calculated and minimized, the values of these displacements are determined from this, etc. This approach is perfectly valid, but does not explain the mechanism that causes the instability in the system. Second, these models describe either a 2×1 structure or a low-temperature structure. None of these models explains simultaneously the existence of different phases and of a transition between them. It remains unclear, for example, why experiments reveal changes in the surface charge and in band buckling when one superstructure changes to another as the temperature is raised. Nor are the causes of the irreversibility of transitions between different superstructures understood. Finally, an explanation is needed for the surface relaxation usually observed together with the reconstruction and due to the change of the distance between the surface atomic plane and the plane that follows it (compared with the bulk interplanar distance).

II. DESCRIPTION OF MODEL

We propose in this paper for the reconstruction of clean faces of semiconducting crystals of mechanism that is free to some extent of the foregoing shortcomings, and also explains the observed surface restructuring caused by atom absorption and laser irradiation. This mechanism is based on the electrostatic interaction between the surface electronic states and the average surface charge and its fluctuations. A similar mechanism was proposed by us earlier²⁹ to explain a similar reconstruction on transition-metal surfaces. We wish to take the following circumstances into account. On the one hand, experimental studies^{9,10,13,14} of the surface-state spectrum show it to have a noticeable dispersion (≈ 0.75 eV). On the other hand, since the surface electrons

are localized near the crystal surface, they are less screened by the bulk electrons, and their electrostatic interaction via the free half-space outside the crystal may be significant.

We attempt to take these circumstances into account in our model and consider various limiting ratios of the size V of the interaction to the width W of the surface band. For $W \gg V$ we take into account the overlap of the electronic states on the surface atoms, but neglect the hybridization of the surface and bulk bands, assuming the direct exchange interaction to be large compared with the indirect one via a bulk band. In the other limiting case $V \gg W$, conversely, hybridization can be taken into account, and the overlap of the surface-states wave functions can be regarded as a perturbation. It is important that both limiting cases lead qualitatively to the same result.

In the chosen model Hamiltonian we wish to take into account also an important feature of a quasi-two-dimensional system located on the surface of a bulky crystal. The experiments referred to above have demonstrated that the surface charge is altered by the surface reconstruction. Clearly, the electric field inside the surface Debye layer can lead to a shift of the surface band, and therefore the occupation of the latter must be determined in a self-consistent manner. "Spillover" of the charge into the interior of a bulky crystal hardly changes the energy of the bulk system, in view of the screening.

The charge that flows over, however, is very small, $\Delta N \sim 10^{10} - 10^{11} \text{ cm}^{-2}$, as can be easily determined from the buckling of the semiconductor bands ($\Delta N \ll N_{\text{sur}} \sim 10^{12} - 10^{13} \text{ cm}^{-2}$). Note that in the bulk impurity density in the investigated semiconducting crystals is as a rule so high that the Fermi level of the electron system cannot change position as a result of the occupation ΔN of the surface band. In Ref. 13 they investigated a p -Si crystal with resistivity $\rho \approx \Omega \cdot \text{cm}$, which corresponds approximately to an impurity-atom bulk density $n \sim 10^{16} \text{ cm}^{-3}$. This compares with $\rho \approx 5 \cdot 10^{-3} \Omega \cdot \text{cm}$ and $n \sim 10^{19} \text{ cm}^{-3}$ for p -Ge (Ref. 30), $\rho \approx 43 \Omega \cdot \text{cm}$ and $n \sim 10^{15} \text{ cm}^{-3}$ for Si (Ref. 31), and others, typical sample thicknesses being $d \sim 5 - 10 \text{ mm}$. We have thus $\Delta N / d \ll n$. In the case of specially prepared very pure Si and Ge samples, on the other hand, it must be borne in mind that at the temperature of the transition from one superstructure to another ($T \approx 500 \text{ K}$) the density of the free bulk carriers greatly exceeds $\Delta N / d$, so that for such a transition the system Fermi level should be regarded as fixed.

It might seem surprising at first glance how such small surface-charge changes ΔN can cause surface reconstruction. We shall explain this right away. The point is that the relatively weak fields produced by such a surface charge penetrate relatively deeply, compared with the atom size, into the interior of the semiconductor ($l_D \sim 10^3 - 10^4 \text{ \AA}$). The electrostatic energy stored in such a "distributed" double layer and amounting to approximately $\pi^2 (\Delta N)^2 l_D / \epsilon$ per unit surface area turns out to be comparable with the energy density of the Coulomb repulsion of the surface electrons $\sim (e^2/a^3) (N_{\text{sur}} / N_{\text{monol}})^{3/2}$, where N_{monol} is the electron surface density, equal to $\sim 10^{15} \text{ cm}^{-2}$. This circumstance will be quantitatively expressed below in Eq. (6).

III. CASE OF WIDE SURFACE BAND

In the band representation, the Hamiltonian of the considered quasi-two-dimensional model is

$$H = \sum_{\mathbf{k}, \sigma} (\varepsilon_{\mathbf{k}} - \tilde{\mu}) a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}, \sigma} + \sum_{\mathbf{q}} V_{\mathbf{q}} \rho_{\mathbf{q}} \rho_{-\mathbf{q}} + g \sum_{\mathbf{k}, \mathbf{q}, \sigma} a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}-\mathbf{q}, \sigma} (b_{-\mathbf{q}}^+ + b_{\mathbf{q}}) + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^+ b_{\mathbf{q}} + V_0 \rho_0 \rho_0 + \hbar \omega_0 c_0^+ c_0 + g_1 \sum_{\mathbf{k}, \sigma} a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}, \sigma} (c_0^+ + c_0). \quad (1)$$

Here $\varepsilon_{\mathbf{k}}$ is the energy of the quasi-two-dimensional surface band; $\tilde{\mu}$ is the Fermi level of the semiconductor; $V_{\mathbf{q}}$ is the electron-interaction matrix element; $V_0 \rho_0 \rho_0$ is the interaction energy of the electrons with the mean double-layer field; $a_{\mathbf{k}} (a_{\mathbf{k}}^+)$ is the operator for annihilation (creation) of electrons with two-dimensional wave vector \mathbf{k} ; $b_{\mathbf{q}} (b_{\mathbf{q}}^+)$ is the operator for annihilation (creation) of phonons of frequency $\omega_{\mathbf{q}}$; g is the electron-phonon interaction constant of the quasi-two-dimensional system; c_0 is the operator of the relaxational displacement of the surface atoms;

$$\rho_{\mathbf{q}} = \sum_{\mathbf{k}, \sigma} a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}-\mathbf{q}, \sigma}, \quad \rho_0 = \sum_{\mathbf{k}, \sigma} a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}, \sigma},$$

where $\rho_{\mathbf{q}}$ is the Fourier harmonic of the density of the electrons with wave vector \mathbf{q} and ρ_0 is the zeroth harmonic of the density operator.

It can be seen that the Hamiltonian (1) consists of two parts. The first is the usual Fröhlich Hamiltonian. The second part takes into account the onset of the surface charge $\langle \rho_0 \rangle$ and contains the energy of the electron interaction with average double-layer field; $\langle \rho_0 \rangle$ is determined in a self-consistent manner. In addition, we have separated in the second part a phonon mode with $q = 0$, which describes the relaxation of the surface atoms and is naturally connected with the surface charge $\langle \rho_0 \rangle$. To take into account the bulk Debye screening of the surface charge in the quasi-two-dimensional electron model, we have put $V_0 = \pi^2 l_D / \varepsilon$, where ε is the bulk dielectric constant of the semiconductor and l_D is the Debye screening length and depends on the temperature and density of the bulk electrons. The quantity V_0 stems from the solution of the three-dimensional problem of surface-charge screening, and is obtained for the electrostatic energy per unit surface area: $U = \pi^2 \sigma^2 l_D / \varepsilon$, where σ is the surface charge density. The effective constant g_1 in the Hamiltonian (1) also includes the energy of the entire Debye layer and describes the interaction between the distributed charge and the field of the atomic displacements produced by the charge in the entire Debye layer.

We consider first the one-dimensional case, after which we discuss the differences that arise in the two-dimensional situation. We diagonalize the Hamiltonian (1) in the self-consistent-field approximation, introducing two order parameters:

$$\Delta(Q) = g \langle \varphi_Q \rangle + V_Q \langle \rho_Q \rangle, \quad \langle \varphi_Q \rangle = \langle b_Q^+ + b_{-Q} \rangle / \omega_Q^{1/2}, \\ \Delta(0) = g_1 \langle \varphi_0 \rangle + V_0 \langle \rho_0 \rangle, \quad \langle \varphi_0 \rangle = \langle c_0^+ + c_0 \rangle / \omega_0^{1/2}.$$

The equations for the Green's functions

$$G_{p', p}(\tau) = -\langle T \tilde{a}_{p'}(\tau) \tilde{a}_p^+(0) \rangle, \\ \tilde{a}_p(\tau) = \exp(\tau H) a_p \exp(-\tau H)$$

take in the self-consistent-field approximation the form

$$\sum_{\nu} (i\omega_{\nu} - H)_{\mu\nu} G_{\nu\lambda} = \delta_{\mu\lambda}. \quad (2)$$

Accordingly, the two self-consistency equations are of the form

$$\Delta(Q) = \left[\frac{2g^2}{\omega_Q} - V_Q \right] 2\pi T \sum_{p'n} G_{p-Q, p}(\omega_n), \quad (3a)$$

$$\Delta(0) = \left[\frac{2g_1^2}{\omega_0} - V_0 \right] 2\pi T \sum_{p'n} G_{p, p}(\omega_n). \quad (3b)$$

Equation (3a) is solved in the case $\Delta(Q) \ll W$ in standard fashion (see, e.g., Ref. 32), except that the chemical potential of the surface-band electrons depends on the quantity $\langle \rho_0 \rangle$ (namely, $\mu = \tilde{\mu} - V_0 \langle \rho_0 \rangle$) which is determined from Eq. (3b).

It follows thus from (3a) that (cf. Ref. 32)

$$\frac{1}{(2g^2/\omega_Q - V_Q) N_0} = \int_0^W d\varepsilon \eta(\varepsilon) \left[\text{th} \frac{E - \mu_-}{2T} + \text{th} \frac{E + \mu_-}{2T} + \text{th} \frac{E - \mu_+}{2T} + \text{th} \frac{E + \mu_+}{2T} \right] \frac{1}{2E}, \quad (4)$$

where

$$E = [\varepsilon^2 \cos^2(qd/2) + \Delta^2]^{1/2}, \quad q = Q - \pi/d, \\ \mu_{\pm} = \mu \pm (W^2 - \varepsilon^2)^{1/2} \sin \frac{qd}{2}, \quad \eta(\varepsilon) = \frac{W}{(W^2 - \varepsilon^2)^{1/2}}, \\ N(0) = \frac{L}{\pi dW},$$

(L is the dimension of the system), and the meaning of (3b) becomes more lucid if it is rewritten in the form

$$\langle \rho_0 \rangle = \left\langle \sum_{\mathbf{k}, \sigma} a_{\mathbf{k}, \sigma}^+ a_{\mathbf{k}, \sigma} \right\rangle = \frac{2L}{\pi} \int d\mathbf{k} n_{\mathbf{k}}. \quad (5)$$

At $T = 0$ the integration in (4) is over a region bounded by the equal-energy surface

$$\varepsilon(\mathbf{k}) = \tilde{\mu} - V_0 \langle \rho_0 \rangle = \mu.$$

Analysis of Eqs. (4) and (5) shows that the system energy is lowered when a self-consistent gap is produced inside the surface band. The electron energy gain is $\sim \Delta^2 \ln(W/\Delta)$ if the gap produced is symmetric about the Fermi level. This result is perfectly identical with that known for Peierls instability. When the position of the gap is changed in a Peierls transition the energy gain is of the same order and the position of the gap is determined by the total number of electrons in the band. In our case displacement of the gap alters the occupation of the band. The system energy depends therefore on

$$\Delta(0) = [-2g_1^2/\omega_0 + V_0] \langle \rho_0 \rangle = -V_0 \text{eff} \langle \rho_0 \rangle,$$

and most favored energy wise is formation of a gap directly above or below the Fermi level, depending on the signs of $\langle \rho_0 \rangle$ and $V_0 \text{eff}$. The occupation of the band is then altered in

such a way that the energy connected with the electrostatic field V_0 and with the relaxation displacement of the atoms, $E_0 \sim V_{0\text{eff}} \langle \rho_0 \rangle^2$, is minimized. Most importantly, the energy gain is proportional to the occupation change $\delta \langle \rho_0 \rangle$, and is consequently proportional to the size of the gap.

$$\delta \langle \rho_0 \rangle \propto \Delta(Q)/V_0. \quad (6)$$

At $\Delta(Q) \ll W$ this energy gain exceeds the usual Peierls value $\Delta^2 \ln(W/\Delta)$, and is the main cause of the reconstruction. In a closed system, the equilibrium value of a parameter such as $\langle \rho_0 \rangle$ would correspond to a minimum of the energy, and the energy change would be quadratic in $\delta \langle \rho_0 \rangle$. In the present case the initial value of $\langle \rho_0 \rangle$ is set by factors external to the surface band, viz., by the Fermi level of the bulk system [see (5)]. Therefore when $\langle \rho_0 \rangle$ is changed in the course of the spectrum reconstruction the energy change is of first order in $\delta \langle \rho_0 \rangle$ or in $\Delta(Q)$. It might seem that the energy could decrease all the way to $\Delta \sim W$. The self-consistency condition (3a) at $V_{Q\text{eff}} \equiv (2g^2/\omega_Q - V_Q) \ll W$, however, limits the gap width to the significantly lower value

$$\Delta(Q) \sim W \exp(-W/V_{Q\text{eff}}). \quad (7)$$

The last circumstance is well known and is due to the fact that if the interaction $V_{Q\text{eff}}$ is small a charge wave $\langle \rho_Q \rangle$ can be produced only if the system susceptibility (the response to a periodic potential) is high enough, but the system susceptibility decreases with increasing gap. For the same reason, onset of the reconstruction considered here in the two-dimensional case requires that the band spectrum contain sections with combined equal-energy surfaces or else saddle points near the Fermi level (at a distance on the order of the gap width).

With rising temperature, the gap $\Delta(Q)$ decreases, so that the occupation $\langle \rho_0 \rangle$ of the surface band is changed together with its position relative to the Fermi level. The Fermi system of the surface will therefore change continuously. This can give rise to a new superstructure if the surface-band spectrum contains other superimposed segments or saddle points. The semiconductor band buckling is then changed, as is also the relaxation displacement of the atoms. We note that, as a result, the total surface charge, including the charges of the surface electrons and of the ion core, can either decrease or increase, depending on the sign of $V_{0\text{eff}}$. In the case of the single-crystal faces Ge(111) and Si(111) the band buckling decreases on going over to the high-temperature superstructure; this is ensured by the positive sign of $V_{0\text{eff}}$, i.e., $2g_1^2/\omega_0 > V_0$.

As indicated above, the surface-layer electrons are less strongly screened and can interact via the free half-space. To cast light on the qualitative situation for a general relation between the system parameters (the magnitude of the interaction and the band width), we consider the restructuring of the upper layer with doubling of the period. The equations for the Green's functions form in this case a closed system and can be easily solved.³³ The self-consistency condition (3a) takes the simple form:

$$\frac{\pi W}{(2g^2/\omega_Q - V_Q)L} = \int \frac{d\varepsilon}{(\varepsilon^2 + \Delta^2)^{1/2} (1 - \varepsilon^2/W^2)^{1/2}} \text{th} \frac{(\varepsilon^2 + \Delta^2)^{1/2}}{2T}. \quad (8)$$

Using expression (8), we can track the behavior of Δ as a function of the ratio of the effective interaction to the band width. Equation (8) has for $T \rightarrow 0$ the solution

$$\Delta = W f(W/V_{Q\text{eff}}), \quad (9)$$

with $f(x) \rightarrow \exp(-x)$ as $m \rightarrow \infty$ [cf. Eq. (7)] and $f(x) \rightarrow q/2x$ as $x \rightarrow 0$. Thus, when the interaction $V_{Q\text{eff}}$ increases the gap increases to a value of the order of W (we shall omit the subscript Q hereafter) at $V_{\text{eff}} \sim W$. With further increase of the interaction ($V_{\text{eff}} \gg W$) we get for the gap $\Delta \sim V_{\text{eff}}$. At $V_{\text{eff}} > W$ the shift of the gap center relative to the Fermi level is of the order of the gap width. In the two-dimensional situation there is no need in this case for overlapping sections of the equal-energy surfaces or for saddle points on the Fermi surface. It should be noted that this treatment of the behavior of Δ is only qualitative, since the self-consistent-field approximation cannot be used in the intermediate range $\Delta \sim W$. This approximation, however, is justified in both limiting cases $W \gg V_{\text{eff}}$ and $W \ll V_{\text{eff}}$. The first case was considered by us above.

IV. CASE OF NARROW SURFACE BAND

We proceed now to the case $W \ll V_{\text{eff}}$. At this ratio of the energy parameters it is correct to consider surface electronic states localized on surface atoms. The overlap of the wave functions of electrons localized on neighboring atoms should be treated as a perturbation. This overlap can be neglected in the zeroth approximation.

We divide arbitrarily the simplest Hamiltonian that describes such a system into four parts:

$$H = H_0 + H_1 + H_2 + H_3. \quad (10)$$

Here H_0 describes states localized on the surface atoms, located near the Fermi level, exchanging electrons with the bulk band, and interacting electrostatically with one another via the free space:

$$H_0 = \sum_{q\sigma} \varepsilon_q n_q + \sum_{q\alpha\sigma} (V_{q,\alpha} a_{q,\sigma}^+ a_{\alpha,\sigma} + \text{H.c.}) + E \sum_{\alpha} n_{\alpha} + \frac{1}{2} \sum_{\alpha \neq \beta} U_{\alpha\beta} (1 - n_{\alpha}) (1 - n_{\beta}), \quad (11)$$

where

$$n_q = \sum_{\sigma} a_{q,\sigma}^+ a_{q,\sigma}, \quad n_{\alpha} = \sum_{\sigma} a_{\alpha,\sigma}^+ a_{\alpha,\sigma}$$

are the occupation-number operators for the bulk system states $|q\rangle$ and for the localized SES $|\alpha\rangle$. Such a Hamiltonian was investigated for adsorbed atoms in Ref. 34, where the correlation energy was assumed large, so that not more than one electron was localized on an atom.

The term H_1 takes into account the fact that the correlation energy U is finite for the surface atoms of the superconducting crystal:

$$H_1 = \sum_{\alpha} U n_{\alpha, \uparrow} n_{\alpha, \downarrow}. \quad (12)$$

A similar analysis was carried out in Refs. 35 and 36. The energy of the electron-phonon interaction in the surface system is taken into account by adding the term H_2 :

$$H_2 = \sum_{\alpha} \frac{M\omega_0^2}{2} \hat{Q}_{\alpha}^2 + \frac{M}{2} \dot{Q}_{\alpha}^2 + \sum_{\alpha} \gamma \hat{Q}_{\alpha} (1 - n_{\alpha}), \quad (13)$$

where the operator \hat{Q}_{α} describes the displacement of the surface atom numbered α ; γ is the electron-phonon interaction constant. The Hamiltonian $H_0 + H_2$ was investigated in Ref. 37. Finally, the term H_3 takes into account, in first-order approximation, the overlap of the wave functions of electrons localized on neighboring atoms³⁶:

$$H_3 = \sum_{\alpha \neq \beta, \sigma} T_{\alpha\beta} a_{\alpha, \sigma}^{\dagger} a_{\beta, \sigma} + \text{H.c.} \quad (14)$$

The Hamiltonian H_0 (Ref. 34) is investigated by the Hartree-Fock method, neglecting the off-diagonal part of the Green's function

$$G_{\alpha\beta} = \langle \alpha | \frac{1}{\varepsilon - H + i\delta} | \beta \rangle.$$

The level density on the atom is given by

$$\rho_{\alpha}(\varepsilon) = -\frac{1}{\pi} G_{\alpha\alpha}(E) = \frac{\Gamma}{\pi} \frac{1}{(\varepsilon - E_{\alpha})^2 + \Gamma^2}, \quad (15)$$

and the self-consistency condition takes the form

$$n_{\alpha} = \int_{-\infty}^{\infty} \rho_{\alpha}(\varepsilon) n_F(\varepsilon) d\varepsilon = \begin{cases} \int_{-\infty}^{-E_{\alpha}} \rho(\varepsilon) d\varepsilon, & T \ll \Gamma, \\ n_F(E_{\alpha}), & T \gg \Gamma, \end{cases} \quad (16)$$

where $n_F(\varepsilon)$ is the Fermi distribution function,

$$E_{\alpha} = E - A + \sum_{\beta \neq \alpha} U_{\alpha\beta} n_{\beta}, \quad A = \sum_{\beta \neq \alpha} U_{\alpha\beta}.$$

This condition can be rewritten in the form

$$E - A + \sum_{\beta \neq \alpha} U_{\alpha\beta} n_{\beta} = \varphi(n_{\alpha}), \quad (17)$$

where

$$\varphi(n) = \frac{1}{2} T \ln[(1-n)/n], \quad T \gg \Gamma, \\ \varphi(n) = \Gamma \operatorname{ctg} \pi n, \quad T \ll \Gamma.$$

It is easily seen that the system (17) has a homogeneous solution $n_{\alpha} = n$, where n is defined by the equation

$$E - A(1-n) = \varphi(n). \quad (18)$$

Since $\varphi(n)$ is a monotonically decreasing function, the solution of (18) is single-valued. The question of existence of other solutions of the system (17) can be answered by linearizing the system near the homogeneous solution (18), $n_{\alpha} = n + m_{\alpha}$:

$$\varphi'(n) m_{\alpha} = \sum_{\beta \neq \alpha} U_{\alpha\beta} m_{\beta}. \quad (19)$$

When the Hamiltonian (10) is used to describe the surfaces Si(111) and Ge(111) one must consider a triangular surface lattice of atoms. Since the interaction between the atoms falls off rapidly with distance on the surface, we consider in the simplest case interaction of only nearest neighbors. We can then introduce four sublattices that consist of atoms of different species (1, 2, 3, and 4 in Fig. 1). Assuming the values of m_i ($i = 1, 2, 3, 4$) equal for each of the sublattices,

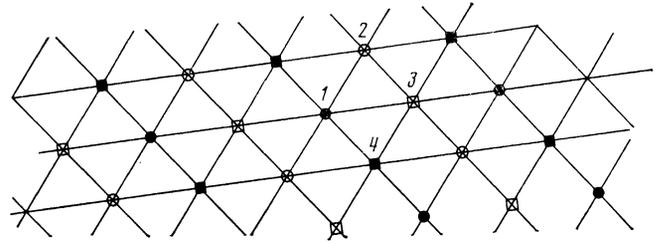


FIG. 1. Structure of surface-atom lattice; 1, 2, 3, and 4 are atoms of four sublattices.

and the values of $U_{\alpha\beta}$ dependent only on the difference between the coordinates α and β , we can rewrite the condition (19) in the form

$$2U(m_2 + m_3 + m_4) = -\lambda m_1, \quad 2U(m_1 + m_3 + m_4) = -\lambda m_2, \\ 2U(m_1 + m_2 + m_4) = -\lambda m_3, \quad 2U(m_1 + m_2 + m_3) = -\lambda m_4, \quad (20)$$

where $U \equiv U - \beta$ for nearest neighbors from two different sublattices, and $\lambda \equiv \varphi'(n) > 0$.

Adding Eqs. (20), we arrive at the requirement

$$m_1 + m_2 + m_3 + m_4 = 0. \quad (21)$$

Thus, solutions with charge that alternates over the sublattices are possible besides the homogeneous ones. In particular, a solution describing the 2×1 structure is possible:

$$m_1 = m_2 = -m_3 = -m_4 \neq 0. \quad (22)$$

Such a state can be energywise more favorable than a homogeneous one. In fact, in the parameter region $2U > \lambda$, whose boundary is determined by the condition (20), the additional energy due to the Coulomb interaction of the charge that alternates over the sublattices is proportional to

$$\sum_{i \neq j} m_i m_j = \frac{1}{2} \left[\left(\sum_{i=1}^4 m_i \right)^2 - \sum_{i=1}^4 m_i^2 \right]$$

and is less than zero for the distribution (22). To investigate the possibility of the appearance of 2×8 and 7×7 structures in such a lattice it is necessary to consider also the interaction of more remote neighbors.

Allowance for the correlations of electrons on an atom, for the interaction of electrons with surface-atom lattice vibrations, and for the overlap of wave functions alters the behavior of the system, but the main conclusion that the charge can alternate remains in force. The charge wave can be accompanied and amplified here by the appearance of an atom-displacement wave³⁷ and a spin-density wave.³⁸ An important result of the study of such a model is the conclusion that the average occupation number of the surface atoms is altered by the reconstruction.³⁷

We see that a system of surface electrons and atoms behaves similarly in both limiting relations of the band width W and the interaction magnitude V : if the surface band is near the Fermi level, charge density waves can appear and accompany the variation of the total surface charge. The energy gained in such a transition is proportional to the change of the surface-band occupation, and the charge flows over into the bulk band as a result of the appearance of the charge-density wave. Only the mechanism that produces

this wave is different: in one case the wave results from Peierls instability, and in the other from a reconstruction of the Jahn-Teller type. The reconstruction is accompanied here by a relaxation in which the change of the distances between the planes is proportional to the change of the surface charge. It seems that this conclusion can be qualitatively generalized to include the entire range of parameter variation.

V. IRREVERSIBILITY OF TRANSITIONS AND THE INFLUENCE EXERTED ON THEM BY ADSORPTION AND EXTERNAL ACTIONS

We have already mentioned in the Introduction that transitions between different superstructures on a semiconductor surface are as a rule irreversible. The reasons may differ. One possible explanation of the metastability of a high-temperature superstructure can be found within the framework of our model.

We point out first that the characteristic times of variation of the surface-band occupation are long compared with the reversible Debye frequencies of the atomic oscillations. The reason is that to go into the interior of the volume the surface-band electrons (holes) must surmount the high energy barrier (~ 1 eV) that separates the surface band from the conduction (valence) band of the crystal. The slowest variable in the free-energy functional of the surface system of electrons and ions is therefore the average occupation $\langle \rho_0 \rangle$ of the surface band. A plot of the free energy F vs this parameter for low temperatures takes the form of a curve with minima that correspond to the charge states of various superstructures and are separated by an energy barrier of order Δ (Fig. 2). As the temperature is raised, the relative positions of the minima change and the height of barrier decreases. If the temperature at which the position of both minima become equal is low enough compared with the height of the barrier, and the fluctuating transition from the high-temperature phase to the low-temperature one can be suppressed.

The system can be transformed from a metastable to a stable state by changing the occupation of the surface band from $\langle \rho_0 \rangle_{II}$ to $\langle \rho_0 \rangle_I$ by external action. This can happen, for example, when the crystal surface absorbs atoms that reverse charge upon absorption. This is a well known phenomenon. For example, when hydrogen is observed by an Si(111) surface the 2×1 structure is changed to 1×1 , and the band buckling changes by approximately 0.11 eV (Ref. 13). The occupation of the surface band can also be altered by laser action on the crystal surface. Experiments have been

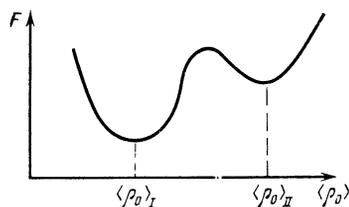


FIG. 2. Dependence of the free energy on the average surface-charge density.

reported³⁸⁻⁴⁰ in which laser action transformed the Si(111) 7×7 structure into 1×1 . It would be equally interesting, however, to use a laser to initiate transitions between the structures 7×7 and 2×1 on an Si(111) surface, or between 2×8 and 2×1 on a Ge(111) surface.

No less interesting a possibility of altering the occupation of a surface band and a corresponding change of the surface structure is offered by application of a strong uniform electric field. This, however, may meet with technical difficulties due to the high field strength needed to displace the band by $\sim W \sim 10^{-1}$ eV ($E \sim W\epsilon/ed_D \sim 10^5 - 10^6$ V/cm).

CONCLUSION

We summarize the main conclusions of the present work.

A possible mechanism is proposed for reconstructing a clean surface of a semiconducting crystal. The mechanism explains the onset of various surface superstructures and the transitions between them at rising temperatures. In this model, the main cause of the structural changes on the surface is the change, made possible by the onset of a charge-density wave, of the charge state of surface levels located near a Fermi-system level. Different limiting ratios of the surface-band width W and the effective electron-electron interaction V are considered ($W \gg V$ and $W \ll V$). In both limiting cases the qualitative behavior of the system, which tends to change its surface charge with rising temperature, is the same, and only the mechanism that produced the charge-density wave is different. The principal energy gain accompanying the reconstruction is connected with the change of the electrostatic field and of the electron-phonon interaction field inside the surface Debye layer.

This analysis agrees with the experimentally observed changes of the band buckling and of the photoelectronic work function in transitions between different superstructures. The proposed model offers a natural explanation for the surface relaxation due to the change of the surface charge in the course of reconstruction.

Several causes of the metastability of high-temperature superstructures are considered. The arguments advanced explain the influence exerted on the structural state of the surface by adsorbed atoms capable of altering the occupation of the surface band of the crystal.

Experiments are suggested in which transitions between different superstructures are initiated by laser and electrostatic action on semiconducting crystal surfaces.

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