Theory of localized states of single impurity centers on a reconstructed surface of diamondlike semiconductors

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We investigated the specific features of chemosorption of a single center on a (2×1) reconstructed (111) face of a homeopolar semiconductor. The crystalline and electric state of the surface is described on the basis of a modified Pendey model. Two variants of the possible locations of an adatom on a substrate are considered. Localized impurity states induced by an adatom in a gap are analyzed in detail. The charge states of the impurity center and the adsorption energy are calculated.

1. INTRODUCTION

Atomically pure surfaces of homopolar semiconductors with silicon structure have already been serving for many years as model objects for theoreticians and experimenters dealing with the interrelation between reconstruction and chemosorption on a crystal surface.[1] Various structural transformations take place on free surfaces of such semiconductors even in the absence of defects or impurities, and their mechanisms and physical characteristics are being investigated quite intensively.[2] The influence of defects and impurities (including chemically active centers sorbed on the surface) leads to additional complications, since it can alter the type of the surface structure and the dependence of its parameters on the degree and character of the coating.

We are interested here, of course, not with so wide a formulation of the problem, but only with a minor aspect connected with a qualitative consideration of the structure of the electronic states on a reconstructed atomically pure surface of a semiconductor, and with the distortion of these states near a single center that simulates an adatom on this surface. It is well known that the surface electronic states are also highly sensitive to singularities of the crystal structure and to its faults. It has thus been established, for example, that a (2×1) doubling of the unit cell takes place on a (111) surface of silicon freshly cleaved in a vacuum (at room temperature) or germanium (below 40 K); further heating causes irreversible structural transformations in the Si(111)–(7×7) and Ge(111)–(2×)8 phases. According to emission and optical measurements,[3] the (2×1) superstructure in Si corresponds, in the spectrum of the surface electronic states, to two subbands separated by an energy gap with $E_g=0.45$ eV. Both subbands are almost entirely contained in a volume band gap, and are radically restructured by a transition from a metastable (2×1) to a stable (7×7) structure.

The determination of the relation between the type of the surface structure and the character of the electron spectrum of the surface states in a crystal is an extremely complicated task. At present, the only more or less satisfactory method is a semiphenomenological selection of the optimal positions of the atoms in the surface layer, followed by calculation of the total energy of the total crystal energy with an aim at minimizing it. Clearly, a self-consistent (with respect to the positions of the atoms in the layers) calculation is practically impossible in such a scheme, and it is necessary to limit oneself to several "reasonable" configurations and to choose the one optimal with respect to energy by calculating the electron-state spectrum corresponding to this configuration. Serious progress was made along these lines in a description of the simplest reconstructed (2×1) phase for the (111) faces of semiconductors with silicon structure, which will be dealt with in the main part of this paper.

The most successful explanation of the entire aggregate of the properties of this phase is provided, at least at present, by the Pendey model[4] (the π-chain model). This model ensures a maximum total-energy gain and explains incontrovertibly the experimental data on the dispersion in filled surface bands and simultaneously the diffraction pattern of the (111)–(2×1) diffraction pattern of silicon,[5] germanium,[6] and diamond.[7] One must bear in mind, however, the noticeable difference between the experimentally obtained gap in the electron spectrum of the surface states and the theoretically predicted values [$E_g^{\exp}\approx0.45$ eV (Ref. 3) and $E_g^{\text{theor}}\approx0.25$ eV (Ref. 8) for Si].

The appearance of an impurity center (adatom) on the surface of a semiconductor can distort substantially the electron-density distribution and the pattern of the electronic states around such a center. One of the causes of this distortion, in the case of a chemosorbed atom, is the onset of a chemical bond between the orbitals of the partially occupied shell of the adatom and the near-surface layers of the semiconductor. A large fraction of the covalence of this bond leads to relative friability of the resultant surface complex, which occupies up to ten lattice constants along (and, generally speaking, into) the sample. As a result the reconstruction pattern becomes very sensitive to the density and type of the adatoms. The inverse is also true, meaning that the reconstruction is accompanied by strong changes of the adsorptivity of the semiconductor surface. Thus, for example, for the (111) face of silicon with a (7×7) superlattice the oxygen-sticking probability is approximately 10 times higher than for the same face with a

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(2×1) lattice.[9] The latter, however, adsorbs more actively hydrogen and chlorine.[10]

It is customary to use in chemosorption theory a semiphenomenological approach wherein the adatom is placed on the substrate in a position such as to close the maximum possible number of broken surface-adatom bonds. This is followed by calculation of the total energy of the resultant complex by using some variant of the cluster approach, and finding the configuration with optimal energy. Obviously, with such an approach it is practically impossible to take correct account of the state of the friable complexes referred to above. Yet the energy scale of the latter (0.01–0.1 eV) is just of importance for the understanding of the picture of the distortion of the surface electron states and of the thermodynamics of the semiconductor surface reconstruction. A similar situation obtains also in the theory of chemosorption on the surface of a simple metal, for which a qualitative theory was proposed long ago, with sufficient account taken of the delocalized character of the distribution of the electron density and the strong covalence of the adatom bond to the substrate.[11] The approach of Ref. 11 is actually based on the Anderson-impurity model, and the adatom is regarded as an isolated center whose states are hybridized with the band states of a nonmagnetic matrix in the surface layer of the metal.

A specific feature of the semiconductor situation is the possible appearance of bound (localized) states of the adatom + matrix complex within the energy gaps of not only volume but also surface states. The origin of these localized states is in fact similar to that of states of deep impurity centers in the bulk of the semiconductor. We describe below the electron structure of a (2×2) complex consisting of an adatom and a reconstructed (111) surface of a silicon-type semiconductor using an approach used successfully in Ref. 12 to develop a theory of deep centers in A^4B^6 semiconductors. We consider several variants of the modified Pendey model, in which account is taken of the fine points of the electron spectrum of the surface states of the crystal structure of the reconstructed layer. We analyze two variants of the possible adatom positions on the semiconductor surface, each corresponding to its own set of matrix elements of the hybridization of the adatom and matrix orbitals.

2. ELECTRON HAMILTONIAN AND GREEN'S FUNCTION OF THE RECONSTRUCTED (111)-(2×1)Si–ADATOM SURFACE

Each atom of the $(111)-(1\times1)$ face of a homeopolar crystal has an outward-directed orbital doubly degenerate in spin, and on the average one valence electron. According to Pendey,[4] the reconstruction $(1\times1)\rightarrow(2\times1)$ involves displacement [both along and across the (111) plane] not only of surface atoms, but also atoms of the next layer, with simultaneous reclosing of the σ-bonds between them. As a result, the surface acquires a new relief in the form of parallel zigzag chains parallel to one another, alternating along the y axis (with periods double the bare one). The schematic form of a reconstructed $(111)-(2\times1)$Si face is shown in Fig. 1. Localized at the nodes of the chain are sp-orbitals, oriented along the normal $\mathbf{z}$ to the crystal surface, of the $|\pi\rangle$ broken bonds, the overlap of which leads to formation of a half-filled metallic π-band with strong dispersion of t in the longitudinal (along the chain) direction $\mathbf{x}$ and with a weak dispersion $t_\perp$ in the transverse $\mathbf{y}$ direction: $t \gg t_\perp$.

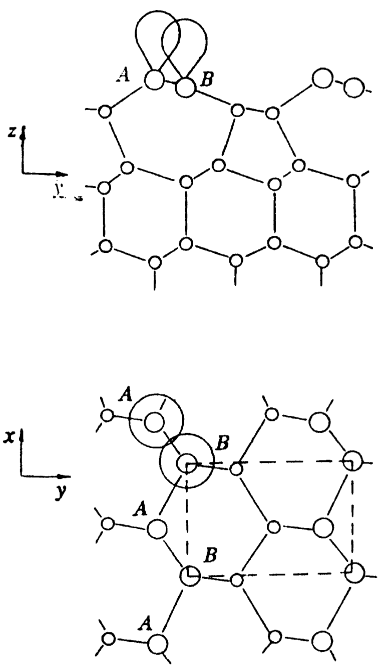

FIG. 1.

In the geometry of an ideal Pendey chain two neighboring nodes of the upper layer A and B per unit cell (shown dashed in the figure) are equivalent. Actually, however, each of them has a somewhat different chemical environment, owing to the low-lying layers. This difference can be characterized by an antisymmetric potential $\Delta_{\text{ion}}(x) = -\Delta_{\text{ion}}(x+a)$ for which we borrow from Ref. 12 the term "ionicity potential." The value of $\Delta_{\text{ion}}(x)$ is formally determined by half the difference between the crystal potentials of a chain made up of links of type A, and a similar chain of type B links.

Beside the chemical dimerization, the non-equivalence of the atoms on the $(111)-(2\times1)$Si surface can be due to distortions of the geometric structure of the π chains as a result of the relative displacement of the sublattices A and B in these chains. The corresponding strain potential $\Delta(x)$ can be represented in the form $\Delta(x) = \Delta_\perp(x) + \Delta_\parallel(x)$. The component $\Delta_\perp(x)$ connected with the transverse corrugation (along the z axis, as shown Fig. 1: side view) has when inverted the same symmetry as the ionicity potential: $\Delta_{\perp,\text{ion}}(x) = \Delta_{\perp,\text{ion}}(-x)$. The displacements of the sublattices in the plane of the (111) face (Fig. 1: top view) are the analogs of the Peierls deformation. The corresponding potential has the property $\Delta_\parallel(-x) = -\Delta_\parallel(x)$. The unit cell of the π-chain is not altered by each of the foregoing variants of dimerization, and the electron spectrum becomes dielectric.

Let us formulate the foregoing in the language of the

π-electron Hamiltonian in the strong coupling approximation:

$$H_\pi=\frac{1}{2}\sum_{j,\sigma} t_{j,j+1}(C_{j\sigma}^+C_{j+1\sigma}+C_{j+1\sigma}^+C_{j\sigma})$$

$$+\Delta_i\sum_{j,\sigma} e^{iQx_j}C_{j\sigma}^+C_{j\sigma}, \tag{1}$$

$C_{j\sigma}^+$ is the creation operator of an electron with spin σ on the jth node of the chain with coordinate $x_j=aj$, $t_{j,\,j+1}=t-\Delta_s\exp iQx_j$ is the overlap integral for neighboring sites; $\Delta_s=\langle\pi|\Delta_\parallel\,(x)\,|\pi\rangle$ is the parameter of the (longitudinal) structural dimerization, and is expressed in terms of the single-site orbital energy; the matrix element $\Delta_i=\langle\pi|\Delta_{\text{ion}}(x)+\Delta_\perp\,(x)\,|\pi\rangle$ will hereafter be referred to as ionicity; $Q=\pi/a$. We neglect the weak coupling of the chains.

We investigate the behavior of an isolated atom on a semiconductor surface in the framework of an Anderson-type Hamiltonian

$$H=H_\pi+H_A+H_{\pi A}+H_{\text{corr}}. \tag{2}$$

Here $H_\pi(1)$ is the unperturbed energy of the π-electrons, while the second term $H_A=\Sigma_\sigma\varepsilon C_{A\sigma}^+C_{A\sigma}$ describes a single isolated center having its own unperturbed energy level ε. The single-defect approximation is valid at a low degree of surface covering, when the average distance between adatoms exceeds the localization scale of their wave functions. The correlation term $H_{\text{corr}}=U_An_{A\uparrow}\;n_{A\downarrow}$ takes into account the Coulomb repulsion of two electrons with opposite spins on the level ε, $n_{A\sigma}=C_{A\sigma}^+C_{A\sigma}$. We use hereafter for H_{corr} the Hartree–Fock approximation, resulting in the substitution $\varepsilon\to\varepsilon_\sigma=\varepsilon+U_A\langle n_{A-\sigma}\rangle$, where $\langle n_{A-\sigma}\rangle$ is the average number of electrons with spin projection per adatom.

It is convenient to use for the single-particle Green's function $G^\sigma(j,1)=\langle T_\tau C_{j\sigma}(\tau)C_{1\sigma}^+(0)\rangle$ of the system the matrix representation G_{nm}^σ, n, $m=1,2,A$. The band indices 1 and 2 correspond to two branches $\pm E(k)$ of the dielectric spectrum of the π chain, which breaks up into two nonequivalent sublattices. The third index pertains to the external atom. In the absence of hybridization ($H_{\pi A}=0$), we have "zero" Green's functions of the form

$$G_{11}^0(K,\omega)=G_{22}^0(K+Q,\omega)=\frac{\omega+t\cos Ka}{\omega^2-E^2(K)},$$

$$G_{12}^0(K,\omega)=G_{21}^{0*}(K,\omega)=\frac{\Delta_i-i\Delta_s\sin Ka}{\omega^2-E^2(K)},$$

$$G_{AA}^{0\sigma}(\omega)=(\omega-\varepsilon_\sigma)^{-1}. \tag{3}$$

A zero denominator in the band components (3) determines the spectrum of the surface quasiparticles $E^2(K)=t^2\cos^2Ka+\Delta_s^2\sin^2Ka+\Delta_i^2$, at the boundaries of which the state density

$$N^0(\omega)=\frac{2}{\pi}\frac{|\omega|\,\theta(\omega^2-\Delta_s^2-\Delta_i^2)\theta(t^2+\Delta_i^2-\omega^2)}{\sqrt{\omega^2-\Delta_s^2-\Delta_i^2}\sqrt{t^2+\Delta_i^2-\omega^2}} \tag{4}$$

has the singularities possessed by one-dimensional systems; $\theta(x)=0$ for $x<0$ and $\theta(x)=1$ for $x>0$. The conduction band is separated from the valence band by an energy gap $E_g=2\sqrt{\Delta_s^2+\Delta_i^2}$.

The Hamiltonian $H_{\pi A}$ describes electron hops from band states of a π-chain to an orbital of the center and back. If the adatom is located exactly above a substrate aadatom with $j=0$, one can take into account for simplicity the bond between the orbitals of just these two atoms (single-site approximation):

$$H_{\pi A}=\frac{V}{\sqrt{2}}\sum_\sigma(C_{A\sigma}^+C_{0\sigma}+C_{0\sigma}^+C_{A\sigma}), \tag{5}$$

V is the matrix element of the interaction between the band and impurity electrons. The solution of the equation $G=G^0+G^0H_{\pi A}G$ takes in this case the form

$$G_{AA}^\sigma(\omega)=G_{AA}^{0\sigma}(\omega)\text{Det}_1^\sigma(\omega)^{-1} \tag{6}$$

for the adatom and

$$G_{nm}^\sigma(j,l;\omega)=G_{nm}^0(j,l;\omega)+\frac{V^2}{2}G_{AA}^{0\sigma}(\omega)\sum_{n',m'}G_{nn'}^0(j,0;\omega)$$

$$\times T_{n'm'}G_{m'm}^0(0,l;\omega)\text{Det}_1^\sigma(\omega)^{-1} \tag{7}$$

for the surface band states with $n,m=1,2$. The matrix T_{nm} has a dimensionality 2×2, and each of its four elements is equal to unity; the denominator is given by

$$\text{Det}\,_1^\sigma(\omega)^{-1}=1-\frac{V^2}{2}\sum_{n,m}G_{nm}^{0\sigma}(0,0;\omega)G_{AA}^0(\omega). \tag{8}$$

The experimental data[2] offer evidence that an adatom (say, Al) is frequently bound to two silicon atoms on the cleavage surface (111)–(2×1), i.e., is in a position of a bridge between neighboring substrate sites. If the adatomic center is located strictly halfway between the "zeroth" $j=0$ and "first" $j=1$ sites of a π chain with $\Delta_\perp=0$, the hybridization matrix elements have a symmetric structure $V_{A0}^s=V_{A1}^s\equiv V$ corresponding in the two-site approximation to the Hamiltonian

$$H_{\pi A}=\frac{V}{2}\sum_\sigma(C_{A\sigma}^+C_{0\sigma}+C_{A\sigma}^+C_{1\sigma}+C_{0\sigma}^+C_{A\sigma}+C_{1\sigma}^+C_{A\sigma}). \tag{9}$$

Any other interstitial position of the adatom on the (x,y) plane or at $\Delta_\perp\neq0$ on the z axis (Fig. 1) is accompanied by an antisymmetric component in the hybridization matrix elements $V_{A0}^{As}=-V_{A1}^{As}$. Nonetheless, we confine ourselves below only to an investigation of the case (9) symmetric with respect to the sites 0 and 1, for which the complete Green's functions take the form

$$G_{AA}^\sigma(\omega)=G_{AA}^{0\sigma}(\omega)\text{Det}_2^\sigma(\omega)^{-1}, \tag{10}$$

$$G_{nm}^\sigma(j,l;\omega)=G_{nm}^0(j,l;\omega)+\frac{V^2}{4}G_{AA}^{0\sigma}(\omega)\sum_{n',m'}[G_{nn'}^0(j,0;\omega)$$

$$+G_{nn'}^0(j,1;\omega)]T_{n'm'}[G_{m'm}^0(0,l;\omega)$$

$$+G_{m'm}^0(1,l;\omega)]\text{Det}_2^\sigma(\omega)^{-1}, \tag{11}$$

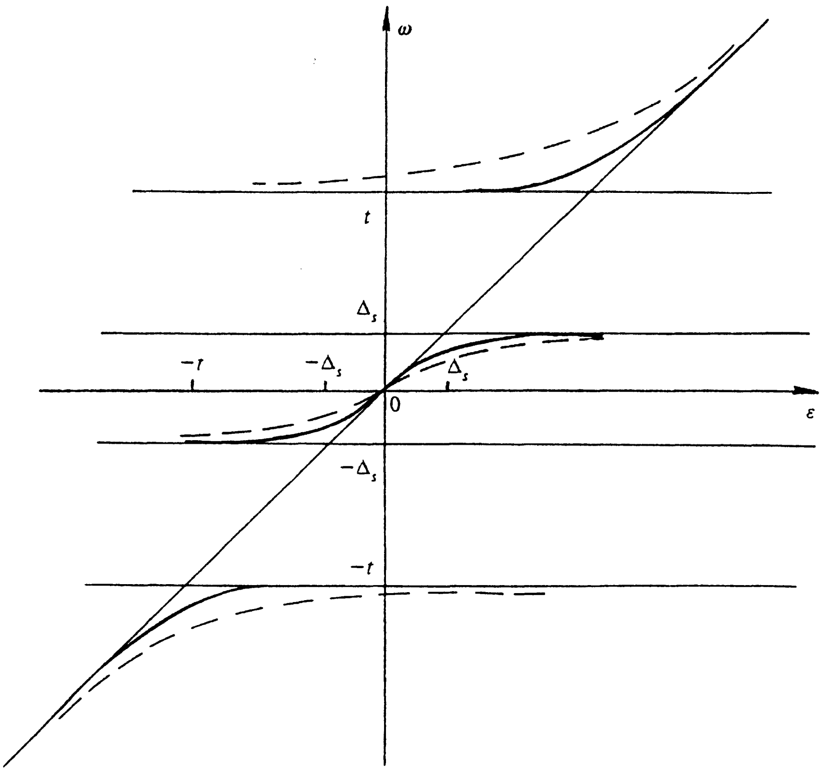

FIG. 2.

$$\mathrm{Det}_2^{\sigma}(\omega)=1-\frac{V^2}{4}\sum_{n'm}\sum_{j,l=0,1}G^0_{nm}(j,l;\omega)G^{0\sigma}_{AA}(\omega). \quad (12)$$

In the Hartree–Fock approximation used here, the entire information on the adsorbate+substrate system is contained in the single-particle Green's functions (6)–(8) and (10)–(12), which depend parametrically on $\langle n_{A\sigma}\rangle$. For a consistent solution of the chemosorption equation one must introduce the self-consistency condition

$$\langle n_{A\sigma}\rangle=\int_{-\infty}^{\mu}N_{A\sigma}(\omega)d\omega, \quad (13)$$

where

$$N_{A\sigma}(\omega)=-\frac{1}{\pi}\,\mathrm{Im}\,G^{\sigma}_{AA}(\omega+i0) \quad (14)$$

is the adatomic density of states for the spin σ, and μ is the chemical potential of the system. The integration in (13) is over both the continuum and the discrete levels. Unfortunately, it is impossible to make the results self-consistent analytically. We confine ourselves therefore first to the case of a nonmagnetic center $\langle n_{A\uparrow}\rangle=\langle n_{A\downarrow}\rangle$ and drop hereafter the spin indices, assuming all the initial levels to be doubly degenerate. Second, we assume (unless otherwise stipulated) that the unrenormalized local level ε has already been renormalized on account of the Coulomb correlations.

The excess charge localized on the eigenstates and the impurity states of the crystal boundary becomes screened in the surface region over a length of the l_d of the Debye length by a charge of the opposite sign, which comes from the bulk bands of the semiconductor. A successive calculation of the charge state of the adsorbate calls also for taking into account the self-consistent bending of the volume bands near the surface and the change of the position of the Fermi level μ relative to the boundaries of the surface band. In the present paper we simply postulate the position of μ inside the forbidden surface band E_g, which agrees with the empirical fact for the atomically pure face[2] (111)–(2×1)Si.

3. LOCALIZED STATES

Hybridization of the surface electronic π states and of the adsorbate states distorts the initial structure of the energy levels. It will be shown below that there exist real frequency values $\omega=\omega_{0,\pm}$ at which the denominator of the Green's function $\mathrm{Det}_{1,2}(\omega)$ vanishes. These values of $\omega_{0,\pm}$ corresponds to electron bound-state energies in the model of a π-chain with adsorbed impurity, and depend on the values of ε and v, on the specific value of the unrenormalized spectrum $E(k)$, and on the position of the adatom. For example, for the model of a one-site defect on a structurally dimerized chain with $\Delta_s=0$, $\Delta_i=0$, we obtain by substituting in (8) the Green's function (3) the equation

$$\frac{V^2}{\varepsilon-\omega}\frac{\omega}{\sqrt{(\Delta_s^2-\omega^2)(t^2-\omega^2)}}=\begin{cases}1, & \omega^2<\Delta_s^2;\\ -1, & \omega^2>t^2,\end{cases} \quad (15)$$

which has three solution for all values of ε and V: one local level is inside the gap $|\omega_0|<\Delta_s$, and the two others above the ceiling of the surface conduction band $\omega_+>t$ and below the valence band $\omega_-<-t$. The possibility of the appearance of levels of type $\omega_\pm$ upon adsorption on a metal-

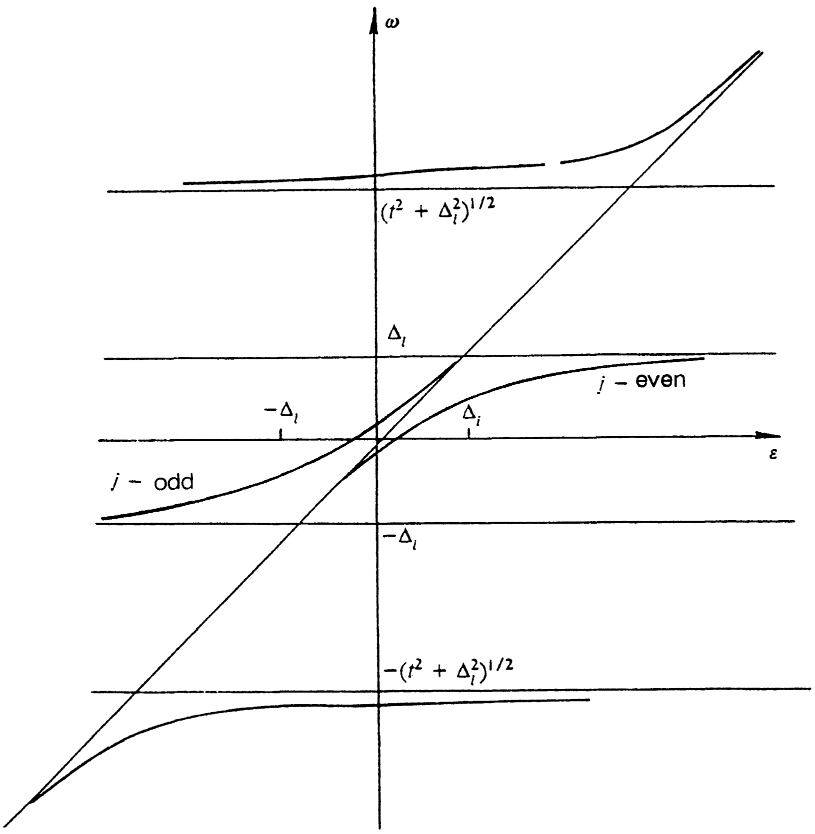

FIG. 3.

lic surface was indicated in Ref. 13. The presence of a localized state with energy ω_0 is inherent in the superconducting structure of a surface state.

A qualitative dependence of the energy $\omega_{0\pm}(\varepsilon,V)$ of hybridized bound states is shown in Fig. 2. When $\varepsilon/t\ll 1$, the level ω_- is close, for sufficiently weak hybridization, to the atomic ε, namely $\omega_-=\varepsilon(1-(V/\varepsilon)^2)$ for $(V/\varepsilon)^2\ll 1$, and the corresponding change of the valence-electron density $\delta\rho_-(j)$ of the electrons in the substrate is characterized by a radius $a_-=2a\ln(2|\varepsilon|/t)$, where $2a$ is the period of the π-chain. Under the condition $\varepsilon>-t$ and $(V^2/t)^2\ll(t+\varepsilon)^2$ we have

$$\omega_-=-t\left(1+\frac{V^4}{2t^2(t+\varepsilon)^2}\right),\quad a_-=2a\frac{V^2}{t(t+\varepsilon)}.$$

If the hybridization constant $(V^2/t)^2\ll\Delta_s^2-\varepsilon^2$ is low, the energy gap acquires a deep level $\omega_0=\varepsilon(1-V^2/t\sqrt{\Delta_s^2-\varepsilon^2})$, corresponding to a charge-density perturbation $\delta\rho(j)$ that falls off exponentially over a distance $a_0=2a(\sqrt{\Delta_s^2-\varepsilon^2}/t)$ from the site with the defect. If the condition $(V^2/t)^2\ll(|\varepsilon|-\Delta_s)^2$, is satisfied for $|\varepsilon|>\Delta_s$, a shallow level

$$\omega_0=\operatorname{sgn}(\varepsilon)\Delta_s\left(1-\frac{V^4}{2t^2(|\varepsilon|-\Delta_s)^2}\right)$$

of a weakly localized state with

$$a_0=2a\frac{V^2\Delta_s}{t^2(|\varepsilon|-\Delta_s)}$$

is split off from the edge of the gap. The π states become most strongly intermixed with the states of the impurity center for the eigenlevel of the last ε close to the surface-band boundaries, where the state density $N^0(\omega)$ has power-law singularities. In the limit $V^2/\Delta_s t\ll 1$ one can obtain the estimates

$$\omega_0=\operatorname{sgn}(\varepsilon)\Delta_s\left(1-\frac{1}{2^{1/3}}\left(\frac{V^2}{t\Delta_s}\right)^{2/3}\right),$$

$$a_0=2^{4/3}a\frac{\Delta_s}{t}\left(\frac{V^2}{t\Delta_s}\right)^{1/3}.$$

A similar distribution of the levels of the localized states is obtained for the bridge coupling (9) between neighboring sites of a π-chain with ionicity. In this case the influence of the potential $\Delta_i\exp iQx_j$ on the electron density in an interstitial position is fully offset. Equation (15) and Fig. 2 remain in force as before, if the notation changes $\Delta_s\rightarrow\Delta_i$ and $t^2\rightarrow t^2+\Delta_i^2$ are made.

One-site hybridization of type (5) of an external atom and a one-dimensional chain with $\Delta_i\neq 0$ and $\Delta_s=0$ leads to the onset of bound-state carriers, with a spectrum given by

$$\frac{V^2}{\varepsilon-\omega}\frac{\omega+\Delta_i e^{iQx_j}}{\sqrt{(\Delta_i^2-\omega^2)(t^2+\Delta_i^2-\omega^2)}}=\begin{cases}1, & \omega^2<\Delta_i^2;\\ -1, & \omega^2>t^2+\Delta_i^2.\end{cases}\tag{16}$$

Evidently the binding energy of the localized state depends on the chain-sublattice in which the adatom lands. There exists an energy threshold $\varepsilon=\varepsilon_t$ of a center on an "even" site j, $\varepsilon_t=-\Delta_i$, below which no localized state is produced in the ionicity gap, and above the level $\varepsilon_t=\Delta_i$ the interval $|\omega|<|\Delta_i|$ contains no state ω_0 in a situation with an adatom on an "odd" site. If $\omega^2>t^2+\Delta_i^2$ the solutions Ref. (16) $\omega_\pm$ exist for all ε and V. A qualitative picture of the levels ω_0 and $\omega_\pm$ is shown in Fig. 3.

For the two-site hybridization model (9) at $\Delta_s\neq 0$, $\Delta_i=0$ the picture of the discrete part of the spectrum of the surface states depends substantially on whether the adatom lands in a "short" or a "long" bridge. In the former case the denominator of the Green's function (12) vanishes under the condition

$$\frac{V^2}{\varepsilon-\omega}\frac{1}{t^2-\Delta_s^2}\left[\frac{t^2+\omega\Delta_s}{\sqrt{t^2-\omega^2}}\sqrt{\frac{\Delta_s-\omega}{\Delta_s+\omega}}\begin{cases}1, & \omega^2>t^2\\ -1, & \omega^2<\Delta_s^2\end{cases}+\Delta_s\right]=0; \tag{17}$$

in the latter case the corresponding condition is obtained by the substitution $\Delta_s\rightarrow-\Delta_s$ in (17).

The eigenvalue equations (15)–(17) of a system with a point defect are similar in form to the analogous equations in Ref. 12, but now the effective scattering potential $U(\omega)=V^2(\varepsilon-\omega)^{-1}$ depends on the frequency ω, making the situation more complicated.

4. SURFACE-STATE DENSITY OF A RECONSTRUCTED SURFACE-ADATOM SYSTEM. CHEMOSORPTION ENERGY

To determine the conditions favoring the formation of a covalence bond between an adatom and a crystal surface we must determine the corresponding change of the system energy W. Averaging the Hamiltonian (2), we obtain at zero temperature

$$W=\int_{-\infty}^{\mu}\Delta N(\omega)(\omega-\mu)d\omega, \tag{18}$$

where the function

$$\Delta N(\omega)=-\frac{2}{\pi}\operatorname{Im}\left[G_{AA}(\omega)-G_{AA}^0(\omega)+\sum_{j,n}(G_{nn}(j,j;\omega)-G_{nn}^0(j,j;\omega))\right] \tag{19}$$

reflects the change of the electron-state density of a surface with a chemosorbed defect. Expression (18) is valid for a fixed value of the chemical potential μ (13), with $\mu^2<\Delta_s^2+\Delta_i^2$ implied. We assume also that all the states are doubly degenerate in spin.

Pay attention first to the situation with a one-site defect in the model of a structurally dimerized π-chain with $\Delta_s\neq 0$ and $\Delta_i=0$. Substituting in (19) the Green's functions (3), (6), and (7) we obtain an explicit expression for the variation $\Delta N(\omega)$. In the energy region ε^2, $\omega^2<\Delta_s^2$ or ε^2, $\omega^2>t^2$ we have

$$\Delta N(\omega)=2[\delta(\omega-\omega_0)+\delta(\omega-\omega_+)+\delta(\omega-\omega_-)-\delta(\omega-\varepsilon)], \tag{20}$$

where the frequencies of the localized states ω_0 and $\omega_\pm$ were defined above [Eq. (15)]. In the region $t^2\gg\varepsilon^2$, $\omega^2\gg\Delta_s^2$ the scattering states become redistributed as follows:

$$\Delta N(\omega)=M(\omega)-\delta(\omega-\Delta_s)-\delta(\omega+\Delta_s)-\delta(\omega-t)-\delta(\omega+t)-2\delta(\omega-\varepsilon). \tag{21}$$

Here the first term

$$M(\omega)=\frac{2}{\pi}\frac{d}{d\omega}\operatorname{arctg}\frac{Z(\omega)}{V^2}, \tag{22}$$

$$Z(\omega)=\frac{(\omega-\varepsilon)\sqrt{(t^2-\omega^2)(\omega^2-\Delta_s^2)}}{|\omega|} \tag{23}$$

represents the delocalized component in the redistribution of the states, and its integration within the limits of the allowed bands, from $-t$ to $-\Delta_s$ or from Δ_s to t yields strictly zero. The four next terms in (21) corresponds to level splitting from the edges of the band continuum (one band from each edge) as a result of electron-impurity scattering by the effective potential $U(\omega)$. As follows from the $\Delta N(\omega)$ structure (20)–(23), the total number of states in the investigated system is preserved when the interaction V is turned on.

It is now easy to write for the chemosorption energy the expression

$$W=2\omega_-+t+\Delta_s-2(\varepsilon-\mu)\theta(\mu-\varepsilon)+2(\omega_0-\mu)\theta(\mu-\omega_0)-\frac{2}{\pi}\int_{-t}^{-\Delta_s}d\omega\operatorname{arctg}\frac{Z(\omega)}{V^2}, \tag{24}$$

the behavior of which can be analyzed in the limit of weak hybridization. If $(|\varepsilon|-\Delta_s)^2\gg(V^2/t)^2$, one can expand the integrand in (24) for large values of the argument $|Z|/V^2\gg 1$, the integral remains convergent and can be expressed as

$$\int_{-t}^{-\Delta_s}d\omega\operatorname{arctg}\frac{Z(\omega)}{V^2}=\frac{\pi}{2}(\Delta_s-t-2(\varepsilon+\Delta_s)\theta(-\Delta_s-\varepsilon))+\frac{2\Delta_sV^2}{(t+\Delta_s)(\Delta_s-\varepsilon)}\left\{K(k)-\frac{2\varepsilon}{\Delta_s+\varepsilon}\Pi(n,k)\right\} \tag{25}$$

in terms of complete elliptic integrals $\Pi(n,k)$ of third kind, with a parameter

$$n=k\frac{\varepsilon-\Delta_s}{\varepsilon+\Delta_s}$$

and modulus

$$k=\frac{t-\Delta_s}{t+\Delta_s},$$

as well as of first order $K(k)$.[14]

In the region, vital to our problem, of the parameters $t\gg\Delta_s$, $|\varepsilon|$, and $|\mu|<\Delta_s$, we use the known[14] expansions for elliptic functions as $k\rightarrow 1$, and obtain from (15) the direct $\omega_0(\varepsilon)$ and $\omega_-(\varepsilon)$ dependences accurate to terms $\sim V^2$ and valid under the condition $(|\varepsilon|-\Delta_s)^2\gg(V^2/t)^2$.

Next, making the corresponding substitutions in (24), we obtain an expression for the chemosorption energy in terms of elementary functions:

$$W=\frac{2V^2}{\pi t}\left[-\ln\frac{4t}{\Delta_s}+\frac{2|\varepsilon|}{\sqrt{\varepsilon^2-\Delta_s^2}}\ln\left(\sqrt{\frac{|\varepsilon|-\Delta_s}{2\Delta_s}}+\sqrt{\frac{|\varepsilon|+\Delta_s}{2\Delta_s}}\right)\right] \tag{26a}$$

for $|\varepsilon|>\Delta_s$;

$$W=\frac{2V^2}{\pi t}\left[-\ln\frac{4t}{\Delta_s}+\frac{2|\varepsilon|}{\sqrt{\Delta_s^2-\varepsilon^2}}\left(\frac{\pi}{2}-\arcsin\sqrt{\frac{\varepsilon+\Delta_s}{2\Delta_s}}\right)\right]$$
$$+2[(\mu-\varepsilon)\theta(\mu-\varepsilon)-(\mu-\omega_0)\theta(\mu-\omega_0)] \tag{26b}$$

for $|\varepsilon|<\Delta_s$.

It can be concluded that the reconstructed surface (111)–(2×1)Si surface is always energywise hospitable to formation of a quasimolecular union of a π-chain with an outer single-site center. If $|\varepsilon|>\Delta_s$, inasmuch as the ionization energy of localized states is $\sim V^4$, an energy gain $W<0$ (26a) is reached only on account of "leakage" of the state density within the limits of the valence bond, and depends on the value $|\varepsilon|$ (but not the sign) of the deviation of the proper level of the adatom from the center of the surface band. The energy released by chemosorption depends, in the limit $\Delta_s/|\varepsilon|\to 0$ (non-dimerized chain) on ε logarithmically, $|W|=(2V^2/\pi t)\ln(2t/|\varepsilon|)$, its value at $|\varepsilon|=\Delta_s$ is $|W|=(2V^2/\pi t)[\ln(4t/\Delta_s)-1]$, and increases substantially at $|\varepsilon|<\Delta_s$, when the localized state ω_0 in the gap [second term of (26b)] comes into play. As seen from (26), the most stable (e.g., to thermal desorption) will be a covalent bond of the surface to an absorbent having a valent orbital with $\varepsilon\cong\mu$. Incidentally, a numerical analysis[13] of chemosorption on a surface with a metallic spectrum has also led to the conclusion that $|W(\varepsilon,\mu)$ reaches a maximum at $\varepsilon\cong\mu$. In our situation, when the resonance $\varepsilon\cong\mu$ is supplemented by a resonance of ε with the edge of the dielectric gap $|\varepsilon|\to\Delta_s$ [but, of course, $(|\varepsilon|-\Delta_s)^2>(V^2/t)^2$] and $|\mu|>|\omega_0|$, we have the estimate

$$|W|\cong-\frac{2V^2}{\pi t}\left(\ln\frac{4t}{\Delta_s}+\frac{\pi\Delta_s}{\sqrt{\Delta_s^2-\varepsilon^2}}\right). \tag{27}$$

The electron-spectrum characteristics associated with the structural doubling of the π chains on the reconstructed (111)–(2×1) face of a homeopolar semiconductor can thus contribute to enhancement of the adsorptivity of the surface.

These conclusions, just as Eqs. (26) with the replacements $\Delta_s\to\Delta_i$ and $t^2\to t^2+\Delta_i^2$, are suitable for the model of a π-chain having ionicity and interacting with a two-site center. If the center is single-site, the situation is in principle different. Let us consider in detail one of two possible versions. Let the local-center state be mixed with a π-orbital of an "even" site of a chain with ionicity Δ_1. The change of the state density of such a system is given by

$$\Delta N(\omega)=2[\delta(\omega-\omega_0)\theta(\varepsilon+\Delta_i)+\delta(\omega-\omega_+)$$
$$+\delta(\omega-\omega_-)-\delta(\omega-\varepsilon)] \tag{28}$$

for the frequencies ε^2, $\omega^2<\Delta_i^2$ and ε^2, $\omega^2>t^2+\Delta_i^2$. The natural frequencies ω_0 and $\omega_\pm$ are determined from Eq. (16), with the solution ω_0 existing only for $\varepsilon>-\Delta_i$;

$$\Delta N(\omega)=M(\omega)-\delta(\omega-\sqrt{t^2+\Delta_i^2})-\delta(\omega+\sqrt{t^2+\Delta_i^2})$$
$$-\delta(\omega-\Delta_i)-2\delta(\omega-\varepsilon) \tag{29}$$

in the interval $t^2+\Delta_i^2\geqslant\omega^2$, $\varepsilon^2\geqslant\Delta_i^2$. The function $M(\omega)$ has the form (22) as before, but now

$$Z(\omega)=(\omega-\varepsilon)\sqrt{\frac{(t^2+\Delta_i^2-\omega^2)(\omega-\Delta_i)}{\omega+\Delta_i}}. \tag{30}$$

Therefore integration of the function $M(\omega)$ yields zero in the conduction band, but in the valence band

$$\int_{-\sqrt{t^2+\Delta_i^2}}^{-\Delta_i}d\omega M(\omega)=-\operatorname{sgn}(\Delta_i+\varepsilon). \tag{31}$$

It follows from (29) that no level separates from the top of the valence band. Substituting (28)–(31) in expression (18), we obtain a general form of the free energy of the system at $|\mu|<\Delta_i$:

$$W=2\omega_-+\sqrt{t^2+\Delta_i^2}+2(\omega_0-\mu)\theta(\mu-\omega_0)\theta(\varepsilon+\Delta_i)$$
$$-2(\varepsilon-\mu)\theta(\mu-\varepsilon)-2\mu\theta(-\Delta_i-\varepsilon)$$
$$+\Delta_i\operatorname{sgn}(\Delta_i+\varepsilon)$$
$$-\frac{2}{\pi}\int_{-\sqrt{t^2+\Delta_i^2}}^{-\Delta_i}d\omega\operatorname{arctg}\frac{Z(\omega)}{V^2}. \tag{32}$$

In the limit of weak hybridization $(|\varepsilon|-\Delta_s)^2>(V^2/t)^2$ the last term of (32) can be expressed in terms of elliptic integrals in the form

$$\int_{-\sqrt{t^2+\Delta_i^2}}^{-\Delta_i}d\omega\operatorname{arctg}\frac{Z(\omega)}{V^2}=\frac{\pi}{2}(\Delta_i-\sqrt{t^2+\Delta_i^2}$$
$$-2(\varepsilon+\Delta_i)\theta(-\Delta_i-\varepsilon))$$
$$+\frac{4V^2}{(\sqrt{t^2+\Delta_i^2}+\Delta_i)(\Delta_i-\varepsilon)}$$
$$\times[\Delta_i\Pi(n,k)-\varepsilon K(k)], \tag{33}$$

$$n=k\frac{\varepsilon-\Delta_i}{\varepsilon+\Delta_i},\quad k=\frac{\sqrt{t^2+\Delta_i^2}-\Delta_i}{\sqrt{t^2+\Delta_i^2}+\Delta_i}.$$

In the range of the plasma parameters $t\gg\Delta_i$, $|\varepsilon|$ and $|\mu|<\Delta_i$ we obtain, proceeding as in the derivation of (26) and using (32), (33), and (16), an expression for the adsorption energy (it can now be easily generalized to include an odd site in a π chain):

$$W=-\frac{2V^2}{\pi t}\left[\ln\frac{4t}{\Delta_i}+2\sqrt{\frac{\varepsilon+\Delta_i(-1)^j}{\varepsilon-\Delta_i(-1)^j}}\ln\left(\sqrt{\frac{|\varepsilon|-\Delta_i}{2\Delta_i}}\right.\right.$$

$$+\sqrt{\frac{|\varepsilon|+\Delta_i}{2\Delta_i}}\bigg)\bigg] \qquad (34a)$$

for $|\varepsilon| < \Delta_i$ and

$$W=-\frac{2V^2}{\pi t}\left[\ln\frac{4t}{\Delta_i}+2\sqrt{\frac{\Delta_i+\varepsilon(-1)^j}{\Delta_i-\varepsilon(-1)^j}}\left(\frac{\pi}{2}-\arcsin\sqrt{\frac{\varepsilon+\Delta_i}{2\Delta_i}}\right)\right]+2[(\mu-\varepsilon)\theta(\mu-\varepsilon)-(\mu-\omega_0)\theta(\mu-\omega_0)\theta(\Delta_i+\varepsilon(-1)^j)] \qquad (34b)$$

for $|\varepsilon| < \Delta_i$.

It follows hence that in the Pendey phase the (111)Si surface is capable of adsorbing point defects with arbitrary values of ε by sites of "positive" ionicity. The centers most strongly interacting with the substrate are those with $\varepsilon \cong \mu > 0$, and when an adatomic level resonates with the bottom of the conduction band $\varepsilon \to \Delta_i$ $(|\varepsilon|-\Delta_i)^2 > (V^2/t)^2$, $\mu > \omega_0$), the energy released is

$$|W| \cong \frac{2V^2}{\pi t}\left(\ln\frac{4t\_}{\Delta_i}+\pi\sqrt{\frac{2\Delta_i}{\Delta_i-\varepsilon}}\right). \qquad (35)$$

The most weakly binding with even sites are centers with $\varepsilon \cong -\Delta_i$:

$$W \cong -\frac{2V^2}{\pi t}\ln\frac{4t}{\Delta_i}.$$

As seen from (34), adatoms with $\varepsilon < \Delta_1$ settle preferably on odd π-chain sites and otherwise, at low degree of coating, they fill the even π-chain sites on a reconstructed (111)-(2×1)Si.

A similar adsorption characteristic should be observed also when an external atom lands in the position of a bridge on a structurally doubled $\Delta_s \neq 0$ π-chain. The role of the site with "positive" ionicity is assumed now by a "long" bridge with "negative" ionicity—a "short" one. A characteristic feature of adsorption on the (111)Si face in the (2×1) phase is the selectivity of the covering of its sites or interstices by impurity atoms occupying a symmetric position on the π chain with doubling.

5. STATE DENSITY AND MEAN NUMBER OF ELECTRONS PER ADATOM

It follows from the preceding section that the adatom interaction with the crystal surface leads both to formation of new hybrid localized states as well as to deformation of a block of surface band eigenstates and broadening of the initial natural level of the isolated center. For the model of a reconstructed $\Delta_s \neq 0$ and $\Delta_i = 0$ surface the density of states (14) and (6) landing on a single-site adatom is of the form

$$N_A(\omega)=\frac{2}{\pi}\frac{V^2}{\varepsilon-\omega}\frac{Z(\omega)}{V^4+Z(\omega)^2}, \qquad (36)$$

where the function $Z(\omega)$ was defined earlier (23). When the state brought to the surface by the impurity has an initial energy in the interval $t-|\varepsilon| \gg V^2/t$ and $|\varepsilon|-\Delta_s \gg V^2/t$, the $N_A(\omega)$ dependence (36) acquires the traditional Lorentzian form of the Anderson-impurity problem. This problem, as applied to chemosorption on a metallic surface, has been well investigated [11,13]. We are interested in the influence exerted on the adsorption process by the band-structure characteristics (3) and (4) of the (111) Si surface, acquired as a result of reconstruction. The most important detail of this process is establishment of a chemical bond between the surface and the adsorbate, and consequently the change of the charge on the center. It is convenient to divide the average number of the electrons on the center into two components, $\langle n_A \rangle = \langle n_A^l \rangle + \langle n_A^b \rangle$, the first due to the presence of a localized state in the gap ω_0 (15):

$$\langle n_A^l \rangle = 2\left(1+\frac{V^2}{t}\frac{\Delta_s^2}{(\Delta_s^2-\omega_0^2)^{3/2}}\right)^{-1}\theta(\mu-\omega_0). \qquad (37)$$

The value of $\langle n_A^b \rangle$ is determined by the contribution of the scattering states to the integral (13) (which can be calculated for Δ_s, $|\varepsilon| \ll t$, $|\mu| < \Delta_s$ by letting the lower limit k go to infinity) and is described by the following system of equations:

$$\langle n_A^l \rangle = 2\left\{\theta(-\Delta_s-\varepsilon)+\frac{V^2}{\pi t}\frac{1}{\varepsilon^2-\Delta_s^2}\left[\varepsilon-\frac{\Delta_s^2}{\sqrt{\varepsilon^2-\Delta_s^2}}\times\ln\frac{|\varepsilon+\sqrt{\varepsilon^2-\Delta_s^2}|}{\Delta_s}\right]\right\} \qquad (38a)$$

at $|\varepsilon| > \Delta_s$, but $(|\varepsilon|-\Delta_s)^2 \gg (V^2/t)^2$ for $\varepsilon < 0$;

$$\langle n_A^b \rangle = \frac{V^2}{\pi t}\frac{1}{\Delta_s^2-\varepsilon^2}\left[\frac{\Delta_s^2}{\sqrt{\Delta_s^2-\varepsilon^2}}\left(\operatorname{arctg}\frac{\sqrt{\Delta_s^2-\varepsilon^2}}{\varepsilon}+\pi\theta(-\varepsilon)\right)-\varepsilon\right] \qquad (38b)$$

at $|\varepsilon| < \Delta_s$, but $(|\varepsilon|-\Delta_s)^2 \gg (V^2/t)^2$ for $\varepsilon < 0$;

$$\langle n_A^b \rangle = \frac{1}{3}+\frac{1}{6\cos(\pi/3)}\left(\frac{V^2}{t\Delta_s}\right)^{2/3}-\frac{2}{9}\left(\frac{2t^2}{\Delta_s V^4}\right)^{1/3}\times(\Delta_s-|\varepsilon|) \qquad (38c)$$

at $(|\varepsilon|-\Delta_s)^2 \ll (V^2/t)^2$ and $\varepsilon < 0$.

Combining (37) and (38), we see that the dependence of $\langle n_A \rangle$ on ε is close in the limit of weak hybridization to the power function $\theta(\mu-\omega_0)$, with a small smearing of the order of V^2/t. In other words, if $\mu < \omega_0$ practically all the valence electrons of the adsorbate flow off into the substrate (donor), and at $\mu > \omega_0$ the orbital of the impurity atom acceptor is almost completely filled.

When an adatom lands on a π-chain node n a model with ionicity $\Delta_i \neq 0$, $\Delta_s = 0$, the distribution $N_A(\omega)$ again satisfies Eq. (36) with the function $Z(\omega)$ from (30) for an even number of the site j [(for odd j it suffices to reverse the sign of Δ_i in 30)]. Proceeding as in the case $\Delta_s \neq 0$ considered above, we obtain the following expression for the average number of carriers on an adatom valence orbital. The contribution of the localized state ω_0 (16) is equal to

$$\langle n_A^l\rangle=2\left(1+\frac{V^2}{t}\frac{\Delta_i(\Delta_i+(-1)^j\omega_0}{(\Delta_i^2-\omega_0^2)^{3/2}}\right)^{-1}\theta(\mu-\omega_0). \quad (39)$$

The delocalized states yield in turn the component

$$\langle n_A^b\rangle=\frac{2V^2}{\pi t}\frac{1}{\varepsilon-(-1)^j}\left[1-\frac{\Delta_i(-1)^j}{\sqrt{\varepsilon^2-\Delta_i^2}}\right.$$

$$\left.\times\ln\frac{|\varepsilon+\sqrt{\varepsilon^2-\Delta_i^2}|}{\Delta_i}\right] \quad (40a)$$

at $|\varepsilon|>\Delta_i$, but $(|\varepsilon|-\Delta_i)^2\gg(V^2/t)^2$ for $\varepsilon<0$;

$$\langle n_A^b\rangle=\frac{2V^2}{\pi t}\frac{1}{\varepsilon-(-1)^j\Delta_i}\left[1-\frac{\Delta_i(-1)^j}{\sqrt{\Delta_i^2-\varepsilon^2}}\right.$$

$$\left.\times\left(\operatorname{arctg}\frac{\sqrt{\Delta_s^2-\varepsilon^2}}{\varepsilon}+\pi\theta(-\varepsilon)\right)\right] \quad (40b)$$

at $|\varepsilon|<\Delta_i$, but $(|\varepsilon|-\Delta_i)^2\gg(V^2/t)^2$ for $\varepsilon<0$;

$$\langle n_A^b\rangle=2\left(1-\frac{V^2}{\pi t\Delta_i}-\frac{2\Delta_i t(\Delta_i-|\varepsilon|)}{V^4}\right) \quad (40c)$$

for even j and

$$\langle n_A^b\rangle=2\left(\frac{1}{3}+\frac{1}{9\cos(\pi/3)}\left(\frac{V^2}{2t\Delta_i}\right)^{2/3}-\frac{2}{9}\left(\frac{t^2}{2\Delta_iV^4}\right)^{1/3}\right.$$

$$\left.\times(\Delta_i-|\varepsilon|)\right) \quad (40d)$$

and for odd j at $(|\varepsilon|-\Delta_i)^2\ll(V^2/t)^2$;

$$\langle n_A^b\rangle 1+\frac{2}{\pi}\operatorname{arctg}\frac{t\sqrt{\varepsilon^2-\Delta_i^2}}{V^2} \quad (40e)$$

for even j and

$$\langle n_A^b\rangle=1+\frac{2}{\pi}\operatorname{arctg}\frac{t(|\varepsilon|-\Delta_i)^{3/2}}{V^2(|\varepsilon|+\Delta_i)^{1/2}} \quad (40f)$$

for odd j at $\varepsilon<-\Delta_i$ but $(|\varepsilon|-\Delta_i)^2\gg(V^2/t)^2$.

Comparing (39) and (40) for different j, we conclude that the average number $\langle n_A\rangle$ of electrons belonging to an adsorbed atom depends on the π-chain site (even or odd) with which it was chemically bound. A similar situation obtains also for a two-site center in the model of a structurally dimerized π chain.

6. CONCLUSION

The here investigated model of chemosorption on a reconstructed face (111)-(2×1) semiconductor with diamond structure takes electron correlations into account neither on π-chain sites nor on an adatom. It is assumed that the electrons move in an electrostatic field of rigorously specified atomic configuration locally perturbed by an impurity center. It is well known, however, that at temperatures $T<T_0\cong 2t\exp(-I/t)$ a low-dimension metal with a half-filled band is unstable to the onset of a spin-density wave (SDW) in weak interelectron interaction $I/T\ll 1$. The most realistic for the (111)-(2×1) surface is a situation in which the spin superstructure is produced against the background of a Pendey atomic corrugation. Thus, it is shown in Ref. 15, in the context of the mean-field theory, that the ground state of a π chain is antiferromagnetic, with a nontrivial mean value $\Delta_t\sim I\langle C_\sigma^+\sigma_{\sigma\sigma'}C_{\sigma'}\rangle$. On the other hand, according to photoelectron-spectroscopy data,[16] an estimate of the Coulomb repulsion of the electrons with orbitals of a broken valence bond on the (111)Si surface yields $I\geqslant 1$ eV, which is of the order of the surface-band width $I/t\sim 1$. In this range of parameters the main contribution to the free energy is made by spin-density fluctuations, and possibly an antiferromagnet is realized on the surface only in the form of a short-range order. Experimental evidence favoring the presence of an SDW on the (111)-(2×1) diamond is provided by Ref. 17.

Another manifestation of the correlation effects is the restructuring (local reconstruction) of the crystalline and electronic environment of the adatomic center. In the above exposition of the features of chemosorption we confined ourselves to the zero-temperature limit and to a low hybridization constant, when one can use the approximation of a "rigid" configuration of the surface temperature. At temperatures close to T_0, however, the electronic subsystem becomes "soft": the valence electrons become redistributed over the correlation-length scale of the order parameter $\Delta_t(x)$ around the atom. The actual structure and amplitude of these static fluctuations of the electron density depend on the charge and magnetic states of the center, and can be calculated self-consistently even in the spirit of the localized SDW theory.[18]

We have determined in this paper the charge on an adatom in a nonmagnetic state. A few words are necessary concerning the possible formation of a magnetic moment $m_A=1/2(\langle n_{A\downarrow}\rangle-\langle n_{A\uparrow}\rangle)$ via chemosorption on a reconstructed surface whose electronic spectrum has a gap, for example of the Peierls type $E_g=2\Delta_s$. It can be shown in the Hartree–Fock approximation that a nontrivial solution $m_A\neq 0$ exists, as is correspondingly a spin splitting $\omega_0\to\omega_0^\sigma$ of the hybrid level, if the condition $\omega_0^\uparrow>\mu>\omega_0^\downarrow$ is satisfied. Equations (37) and (38b) hold then if $|\varepsilon_\sigma|<\Delta_s$ and by neglecting terms of order $V^2/t\Delta_s\ll 1$ we obtain the estimate $2m_A=\langle n_{A\downarrow}\rangle=1$, $\langle n_{A\uparrow}\rangle=0$ and the splitting $\omega_0^\uparrow-\omega_0^\downarrow=U_A$.

We consider in conclusion a number of problems connected with the applicability of our model to specific objects; the surface (111) of Si or C (diamond), chemosorbed by H, by alkali metals, or by halides. The first group of questions deals with how suitable the approximation of isolated Pendey chains is for the calculation of the structure of local levels of adatoms. According to band calculations (see, e.g., Ref. 19) for Si and C, and to qualitative estimates in the style of Ref. 20, the π-chain overlap integral $t_\perp$ is small not only compared with intrachain t, but also with the quantity Δ($t_\perp/t\sim 0.05$–0.1, $t_\perp/\Delta\sim 0.1$–0.3, $t\sim 1$–2 eV, $\Delta\sim 0.3$–0.5 eV). The deformation of the square-root singularity in the density of states on the edges of the gap influences substantially only the structure of shallow levels with ionization energies $|\omega_0-\Delta|\ll t_\perp$.

The more serious approximation is connected with disregard of the overlap of the π-orbitals of the chains with the orbitals of the second and farther layers of the substrate. In the approximation when the partial density of states $N_2(\omega)$ of the second layer is assumed equal to the bulk $N_V(\omega)$, an estimate of the smearing of the electron state on a π-chain due to hybridization with the bulk states yields $v(\omega)\sim t_z^2 N(\omega)$, where t_z is the overlap of the integral of the π-orbital with the orbital of the second layer. Owing to the directional character of the *sp*-bonds we have $t_z\sim t$, and therefore only the smallness of $N(\omega)$ can justify the use of the chain approximation. In the case of Si and C (diamond) the zone of the surface π-orbitals lies entirely inside the bulk forbidden band, where $N(\omega)=0$. In Ge at the same time the π-orbital zone overlaps the bulk valence band in an appreciable energy interval (of the order of t), so that the square-root singularity in the state density becomes apparently smeared out at energies higher than Δ. It seems thus that the situation in Ge cannot be adequately described by our model.

The parameter V/t as estimated by the procedure of Ref. 20 is equal in the above systems to 0.5–1.0 (recall that we are dealing with overlap of outer *s*- and *p*-shells). The energy ε can be roughly estimated from the ionization energy table[20] for the upper valence states. This system yields for the case of Si: $\varepsilon<0$, $|\varepsilon|\sim 5$–7 eV (hydrogen and halogens) and $\varepsilon>0$, $\varepsilon\sim 1$–3 eV (alkali metals), whereas for the case of C we have $\varepsilon<0$, $|\varepsilon|\sim 2$–4 eV (hydrogen and halogens) and $\varepsilon>0$, $\varepsilon\sim 3$–5 eV (alkali metals). According to these estimates, the most promising from the standpoint of observing local level within the surface-state gap are the system Na/Si(111) and H/C(111). In these systems the level ionization energy is ~ 0.1 eV, and in the remaining ones it is lower by almost an order of magnitude, so that their identification has low probability.

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