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# Electron states of atoms in monolayers adsorbed on silicon carbide

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Estimates of charge transfer between adsorbate monolayer and SiC substrate based on account of the dipole-dipole repulsion and exchange interactions are presented. It is demonstrated that all the interaction channels lead to adlayer depolarization. Role of the band and local adatoms states are analyzed. Methods of experimental verification of the obtained results are proposed.

**Keywords:** dipole-dipole interaction, direct and indirect exchange couplings.

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## 1. Introduction

Despite a long history of study, silicon carbide, characterized by a large number of polytypes with significantly different forbidden bands and high resistance to aggressive media, still remains an attractive object of research [1–4]. It should be emphasized, however, that the adsorption capacity of SiC polytypes was relatively poorly studied, despite the importance of this characteristic from both fundamental and technological points of view. In previous papers we considered the adsorption of single atoms of I, VII [5] and II, VI [6] groups on C- and Si-faces of cubic and basic hexagonal polytypes of silicon carbide. Here we discuss the finite concentrations of adatoms, i.e. adsorbed layers (adlayers). In this case, it is convenient to introduce the degree of coverage $\Theta = N/N_{\mathrm{ML}}$, where $N(N_{\mathrm{ML}})$ is the concentration of adsorbed particles in the layer (monolayer).

The problem of adsorption at a finite concentration of adatoms involves consideration of the interaction between them. There are three main channels for such interaction [7]. If a charge transfer occurs between the layer and the substrate, then a dipole-dipole interaction occurs between the adatoms. The other two channels are exchange interactions: the indirect exchange of adatoms through the electronic states of the substrate, and the direct exchange that occurs when the orbitals of neighboring adatoms overlap. Since the adsorption of single atoms of I, II, VI, and VII groups on SiC leads to a significant charge transfer [5,6], let us begin with discussion of the dipole-dipole interaction. Further, we will assume that all adatoms are identical and occupy equivalent positions on the surface of the substrate, so that dipole-dipole repulsion acts in the adlayer.

## 2. Dipole-dipole repulsion

The influence of the dipole-dipole interaction on the electronic state of atoms in layers on a semiconductor was studied by us in the paper [8]. According to the results of papers [5,6], the adatom occupation number is $n = n_b + n_l$, where $n_b$ is the band contribution, which at zero temperature is equal to the contribution of the valence band $n_v$, $n_l$ is the contribution of local states with energies $\omega_l$ lying in the energy gap of the substrate. As shown at zero temperature in the paper [8], the occupation numbers in the adlayer are:

$$n_v(\Theta) = \frac{1}{\pi}\,\mathrm{arcctg}\,\frac{\varepsilon_a(\Theta)+R}{\Gamma}, \qquad R = \frac{E_g}{2}\sqrt{1+\frac{4\Gamma}{\pi E_g}}, \tag{1}$$

$$n_l(\Theta) = \nu_l(\Theta)\cdot\Theta_H\big(E_{\mathrm{F}}-\omega_l(\Theta)\big),$$

$$\nu_l(\Theta) = \left(1+\frac{\Gamma}{\pi}\frac{E_g}{(E_g/2)^2-\omega_l^2(\Theta)}\right)^{-1}. \tag{2}$$

Here $E_g$ is the energy gap width of the substrate, $\Gamma$ is the half-width of the quasi-level of isolated adatom, $\varepsilon_a(\Theta) = \varepsilon_a - \varepsilon_{dip}(\Theta)$, $\varepsilon_{dip}(\Theta) = \Theta^{3/2}\xi Z_a(\Theta)$, $\varepsilon_a$ is energy level of isolated adatom, $\xi = 2e^2d^2N_{\mathrm{ML}}^{3/2}A$ is dipole interaction constant, $e$ is elementary charge, $d$ is adsorption bond length, $A \sim 10$ is factor weakly dependent on adlayer geometry, $\Theta_{\mathrm{H}}(\ldots)$ is Heaviside function, $Z(\Theta)$ is adatom charge in the adlayer, equal to $1-n(\Theta)$, if the adatom level is initially (before adsorption) filled (donor adatoms), and $-n(\Theta)$ if the adatom level is initially empty (acceptor adatoms). A general analysis of the dependencies (1) and (2) was carried out in the paper [8]. Here we address numerical estimates of the values $n_{\mathrm{ML}} = n(\Theta = 1)$ and $Z_{\mathrm{ML}} = Z(\Theta = 1)$ for specific adsorption systems.

As adsorbates let us consider Na and Cl atoms, which are typical donor and acceptor. During adsorption on Si- or C-faces of silicon carbide, the area per atom is $S = 3\sqrt{3}\,a^2/4$, where $a$ is the distance between the nearest neighboring adatoms. Because $N_{\mathrm{ML}} = 1/S$[1], assuming for simplicity $a = 2$ Åwe obtain $N_{\mathrm{ML}} \approx 17.5 \cdot 10^{-2}\,\text{Å}^{-2}$. Since for the C-face $d_{\mathrm{Na}} = 2.64$ and $d_{\mathrm{Cl}} = 1.76$ Å [5,9,10], we get $\xi_{\mathrm{Na}} \approx 100$ and $\xi_{\mathrm{Cl}} \approx 50$ eV. For Si-face $d_{\mathrm{Na}} = 3.05$, $d_{\mathrm{Cl}} = 2.17$ Å and $\xi_{\mathrm{Na}} \approx 140$, $\xi_{\mathrm{Cl}} \approx 70$ eV. In accordance with the results of paper [5] we have $\Gamma = 0.63(3.03)$ and $0.35(1.31)$ eV for C- and Si-faces during the adsorption of sodium (chlorine). If the substrate is polytype $6H$-SiC ($E_g = 3$ eV) $p$-, then when sodium is adsorbed on C-face we have $\varepsilon_a = 1.14$ eV, $\omega_l = 0.86$ eV, $Z_0 = Z(\Theta = 0) = Z^{>} = 0.93$ (symbol $>$ ($<$) means that the local levels lie above (below) the Fermi level, and therefore are empty (filled)); during adsorption on Si-face we have $\varepsilon_a = 1.00$ eV, $\omega_l = 0.86$ eV, $Z_0 = 0.96$ (the energy is counted from the center of the forbidden band) [5]. When chlorine is adsorbed on the C-face, $\varepsilon_a = -0.72$ eV, $\omega_l = -0.32$ eV, $Z_0 = Z(\Theta = 0) = Z^{<} = -0.78$; during adsorption on Si-faces we have $\varepsilon_a = -0.33$ eV, $\omega_l = -0.21$ eV, $Z_0 = -0.86$ [5][2], where $6H$-SiC has $n$-conductivity. Here, doping type was selected due to large values of $|Z_0|$ to demonstrate depolarization of adatoms with $\Theta$ increasing. For adsorption on metals and semiconductors, the dependence $|Z(\Theta)|$ is either a smoothly decreasing function (in this case, the slope $|\partial Z(\Theta)/\partial\Theta|$ also decreases), or a function with a relatively weak minimum with intermediate coatings $\Theta^* \sim 0.5$ [7,11]. Further, we restrict ourselves to the estimates $n_{\mathrm{ML}} = n(\Theta = 1)$ and $Z_{\mathrm{ML}} = Z(\Theta = 1)$.

Since the dipole interaction constant $\xi$ is the largest energy value of the problem, we assume that $\xi|Z_{\mathrm{ML}}| \gg |\varepsilon_a + R|, \Gamma$. For sodium, from (1) and (2) we find, respectively,

$$n_v^{\mathrm{ML}} \sim 1 - \Gamma/\pi\xi Z_{\mathrm{ML}}, \quad n_l = 0. \tag{3}$$

Since $\upsilon_l^{\mathrm{ML}} \sim 0$, we get $Z_{\mathrm{ML}} \sim \sqrt{\Gamma/\pi\xi} \sim 0.04$ during adsorption on C- and Si-faces of $6H$-SiC of $p$-type. Thus, a strong depolarization takes place, as a result of which the adsorbed Na ion loses almost all of its charge. Obviously, the same result will also take place in the case of sodium adsorption on polytype $p$-$4H$-SiC ($E_g = 3.23$ eV). Moreover, the ordered estimates (3) and the conclusion about strong depolarization can also be applied to other alkali and alkaline earth metals (see papers [5,6]).

Let us now turn to the adsorption of chlorine on C- and Si-faces of the $6H$-SiC of $n$-type. Assuming again that $\xi|Z_{\mathrm{ML}}| \gg |\varepsilon_a + R|, \Gamma$, we get

$$n_v^{\mathrm{ML}} \sim -\Gamma/\pi\xi Z_{\mathrm{ML}},$$

$$\upsilon_l^{\mathrm{ML}} \sim (2\pi E_g/\Gamma)\exp(-\pi\xi Z_{\mathrm{ML}}/\Gamma). \tag{4}$$

Hence $n_v^{\mathrm{ML}} \sim -2 \cdot 10^{-2}/Z_{\mathrm{ML}}$, $n_l^{\mathrm{ML}} \sim 0.8 \cdot 10^{-2}$ and $Z_{\mathrm{ML}} \sim -\sqrt{\Gamma/\pi\xi} \sim -0.15 \sim 0.15$ (C-face) and $n_v^{\mathrm{ML}} \sim \sim -6 \cdot 10^{-3}/Z_{\mathrm{ML}}$, $n_l^{\mathrm{ML}} \sim 0$, so $Z_{\mathrm{ML}} \sim -\sqrt{\Gamma/\pi\xi} \sim 0.08$ (Si-face). Thus, a significant depolarization takes place, and, as in the case of alkali metals, the charge of monolayer atoms is determined by the predominant contribution of the valence band. The made ordered estimates can be extended to the $4H$-SiC substrate of $p$-type and to the adsorption of strontium and barium. Also note that the qualitative conclusions about the depolarization of adatoms do not depend on the type of substrate conductivity.

The energy of the adatom bonding to the substrate (adsorption energy) at $\Theta = 1$ is equal to $E_{\mathrm{ads}}^{\mathrm{ML}} = E_{\mathrm{ion}}^{\mathrm{ML}} + E_{\mathrm{met}}^{\mathrm{ML}}$, where the estimates of the ionic and metallic components are, respectively

$$E_{\mathrm{ion}}^{\mathrm{ML}} = -\frac{(Z_{\mathrm{ML}}e)^2}{4d}, \quad E_{\mathrm{met}}^{\mathrm{ML}} = -\frac{\hbar^2}{2mr_a^2}\left(1 - \frac{r_a^2}{d^2} + \frac{r_a^2}{a_0^2}\right). \tag{5}$$

In (5) for $E_{\mathrm{met}}^{\mathrm{ML}}$ it is taken into account that, in contrast to the adsorption of a single atom, where electron can only pass into the bulk of the substrate, for $\Theta = 1$ additional delocalization of electrons in the plane of the adlayer is possible. On passing from the adsorption of a single atom to a monolayer, the change in the adsorption energy is $\delta E_{\mathrm{ada}} = \delta E_{\mathrm{ion}} + \delta E_{\mathrm{met}}$, where $\delta E_{\mathrm{ion}} = e^2(Z_0^2 - Z_{\mathrm{ML}}^2)/4d^2$ and $\delta E_{\mathrm{met}} = -\hbar^2/2md^2$. Introduce relationship $\beta = -\delta E_{\mathrm{ion}}/\delta E_{\mathrm{met}} \sim d(Z_0^2 - Z_{\mathrm{ML}}^2)$, where $d$ is measured in Å. For $\beta < 1$, the energy $E_b = -E_{\mathrm{ads}}$ of adatom bonding with substrate in monolayer is greater than that of a single atom. For Na adsorption on $p$-$6H$-SiC we have $\beta \sim 2$ (C-face) and $\sim 3$ (Si-edge); for Cl adsorption on $n$-$6H$-SiC we have $\beta \sim 1$ (C-face) and $\sim 1.50$ (Si-edge).

## 3. Exchange interactions

At high (close to monolayer) coverages, when the electron shells of neighboring adatoms overlapping occurs, the electron gets the opportunity to move from adatom to adatom [7]. Such interatomic bond is called direct or kinetic exchange. As in the previous Section, we consider a monolayer of adatoms located in top positions and forming a hexagonal two-dimensional (2D) lattice on the $(0001)$ and $(000\bar{1})$ faces of silicon carbide. Within the framework of the adsorption approach and the low-energy approximation the density of states of such lattice is given by expression (10) from paper [12]. This expression, however, is rather large,

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[1] It should be noted that $N_{\mathrm{ML}}$ and $\Theta$ are ill-defined parameters. Therefore, researches practically refused from their use and prefer to talk about the dose of irradiation of the substrate surface by atoms. In theories from the first principles various geometries of the adlayer are discussed, while it is assumed that its structure is comparable with that of the substrate. In the model approach, one often takes $N_{\mathrm{ML}} \sim 1/\pi r_a^2$, where $r_a$ is the atomic radius of the adsorbate. A similar estimate is also valid for disparate structures of the adlayer and the substrate face.

[2] All charges of adatoms of II and VI groups are negative by definition. In the Tables of papers [5,6] for these groups $|Z^{>(<)}|$ are given instead of $Z^{>(<)}$ as in the text. An exception is the data on halogens adsorption on Si-face $3C$-SiC [5], where exactly $Z^{>(<)}$ values are given. It should also be taken into account that in the formulas (5) of papers [5,6] in the denominators of the multiplier before the brackets $r_a^2$ are used, not $d^2$.

and it seems impossible to obtain the occupation number of the lattice adatom in analytical form using it. Therefore let's ruse simplifications.

Using expression (6) from paper [13], the Green's function for adatom of epitaxial hexagonal 2D lattice can be written as

$$G(\omega,\mathbf{q}) = g_a(\omega)[1 - g_a^2(\omega)t^2 f^2(\mathbf{q})]^{-1}. \tag{6}$$

Here $f(\mathbf{q}) = 3|\mathbf{q}|a_0/2$ (low energy approximation), $\mathbf{q}$ is 2D wave vector counted from the Brillouin K band point of 2D hexagonal lattice, $\omega$ is energy variable, $t$ is electron hopping energy between nearest neighbors in the lattice, $g_a(\omega) = \big(\omega - \varepsilon_a - \Lambda(\omega) + i\Gamma(\omega)\big)^{-1}$ is single adatom Green's function, $\Lambda(\omega)$ and $\Gamma(\omega)$ is shift and broadening functions of atomic level $\varepsilon_a$. As in [5,6], to describe the density of states of the substrate $\rho_{\text{sub}}(\omega)$, we will use the Haldane-Anderson model, according to which $\rho_{\text{sub}}(\omega) = \rho_s$ for $|\omega| \geq E_g/2$ and $\rho_{\text{sub}}(\omega) = 0$ for $|\omega| < E_g/2$, where the energy zero is placed at the center of the forbidden band. Then $\Gamma \equiv \pi V^2 \rho_s = \text{const}$ and $\Lambda(\omega) = (\Gamma/\pi)\ln|(\omega - E_g/2)/(\omega + E_g/2)|$ and $\Gamma \equiv \pi V^2\rho_s$ $= \text{const}$, where $V$ is matrix element of substrate-adatom interaction. Since the maximum value of $|\mathbf{q}|$ is equal to the cutoff vector $q_c = 2\sqrt{2\pi}/a_0\sqrt{3\sqrt{3}} \approx 2.2/a_0$ [14], the maximum value of the function $f(\mathbf{q})$ is $f_{\max} = f(q_c)$ $= \sqrt{2\pi/\sqrt{3}} \approx 1.90$, average value $\bar{f} = f(q_c/2) \approx 0.95$. On the other hand, the Green's function of the adsorbed dimer is (see [15])

$$G_{\dim}(\omega) = g_a(\omega)[1 - g_a^2(\omega)t^2]^{-1}, \tag{7}$$

so $G(\omega) = G(\omega, q_c/2) \approx G_{\dim}(\omega)$. Thus, in order to simplify subsequent estimates (eg, occupation numbers), the epitaxial layer can be modeled with a dimer.

The Geen's functions of the dimer correspond to the density of states

$$\widetilde{\rho}(\omega) = \frac{1}{2}\,[\rho_-(\omega) + \rho_+(\omega)],$$

$$\rho_\pm(\omega) = \frac{1}{\pi}\frac{\Gamma(\omega)}{(\omega - \varepsilon_a - \Lambda(\omega))^2 + \Gamma^2(\omega)}. \tag{8}$$

Here and further, the tilde denotes all values related to the lattice. Then it can be shown that $\widetilde{n}_{v(l)} = (n^-_{v(l)} + n^+_{v(l)})/2$, where

$$n_v^\pm = \frac{1}{\pi}\operatorname{arcctg}\frac{\varepsilon_a + R \pm t}{\Gamma}, \qquad n_l^\pm = v_l^\pm \cdot \Theta_H(E_{\text{F}} - \omega_l^\pm),$$

$$v_l^\pm = \left(1 + \frac{\Gamma}{\pi}\frac{E_g}{(E_g/2)^2 - (\omega_l^\pm)}\right)^{-1} \tag{9}$$

and values $\omega_l^\pm$ are determined from the equations $\omega - \varepsilon_a \mp t - \Lambda(\omega) = 0$ for energies $|\omega| < E_g/2$.

Let us reconsider the adsorption of Na and Cl on 6*H*-SiC of *p*- and *n*-types of conductivity, respectively. In accordance with the data of paper [16] for $\sigma$-bonds *s*-orbitals of sodium atoms $t = 2.82\,\text{eV}$ and *p*-orbitals of chlorine atoms $t = 4.74\,\text{eV}$. Calculation by formulas (9) gives for the lattice of sodium atoms formed on *p*-6*H*-SiC the values $\widetilde{Z} \sim 0.7$ and 0.6 for C- and Si-faces, respectively, which are significantly less than the values $Z_0 \sim 0.9$ and 1.0 for a single sodium atom adsorbed on the same faces. For the lattice of chlorine atoms formed on *n*-6*H*-SiC, $\widetilde{Z} = -0.6$ and $-0.5$ for C- and Si-faces, respectively, which is less in modulus than the values $Z_0 = -0.8$ and $-0.9$ for a single chlorine atom adsorbed on the same faces. Thus, in the considered cases, direct exchange leads to a significant depolarization of adatoms.

Indirect exchange is a virtual interatomic transitions of electrons through the states of the substrate [7]. In contrast to the dipole interaction, which occurs only when the adatoms have a charge, and direct exchange, which manifests itself only at $\Theta \to 1$, indirect exchange is always present. Here we will not turn to the general theory, but consider adsorbed „dimer", whose atoms are connected not by direct (as in a actual dimer), but by indirect exchange. As shown in paper [17], the Green's function of such „dimer" is determined by expression (7) when the hopping energy $t$ is replaced by

$$t_{\text{indir}} = \left|V^2 \sum_{\mathbf{k}} \frac{\exp(i\mathbf{kr})}{\omega - \varepsilon_{\mathbf{k}} + i0^+}\right|, \tag{10}$$

where $\mathbf{k}$ and $\varepsilon_{\mathbf{k}}$ are the wave vector and the energy of the substrate electron, $|\mathbf{r}| = a_0$. Using the estimates of paper [17], we assume $t_{\text{indir}} \approx 2V^2/W$, where $W$ is width of SiC valence band. Since $\Gamma = \pi V^2\rho_{\text{sub}} \approx 4\pi V^2/W$, we get $t_{\text{indir}} \approx \Gamma/2\pi$. Then for the adsorption of sodium atoms on 6*H*-SiC we obtain $t_{\text{indir}} \approx 0.10$ (C-face) and 0.06 eV (Si-face); for adsorption of chromium atoms $t_{\text{indir}} \approx 0.48$ (C-face) and 0.21 eV (Si-face). So $t_{\text{indir}}/t \ll 1$. Nevertheless, it is clear that the indirect interaction, like the direct one, leads to the depolarization of adatoms.

## 4. Conclusion

In the present paper we used numerous simplifications, both during parameters estimation, and models selection. Moreover, we considered each adatoms interaction channel as acting independently of other channels. This approach made it possible to demonstrate that dipole forces are the dominant cause of depolarization. Therefore, results provided by us can be considered as semi-quantitative only. These results, however, can be quite simply (in principle) verified experimentally. Indeed, the change in the work of the adsorption system yield, given by the expression $\Delta\phi(\Theta) = -\Theta\Phi Z(\Theta)$, where $\Phi = 4\pi e^2 dN_{\text{ML}}$, is uniquely related to the charge of the adatom. Thus, for $\Theta \ll 1$, the value $\partial\Delta\phi(\Theta)/\partial\Theta$ allows one to estimate the charge of a single adatom $Z_0$, and the value $\Delta\phi(\Theta = 1)$ gives information about the charge $Z_{\text{ML}}$. Moreover, the ratio $Z_0/Z_{\text{ML}}$ can be obtained purely empirically without use of additional assumptions about the distance $d$ between the substrate and the adlayer. Further, the value $\Delta\phi(\Theta)$ is related to the change in the surface conductivity of the substrate $\Delta\sigma(\Theta)$ by the relation $|\Delta\sigma(\Theta)/\Delta\phi(\Theta)| = \mu/4\pi d$, where $\mu$ is the carrier mobility, which, as estimates show, weakly depends on $\Theta$ (see [18] and references given there). Therefore, to check obtained results, instead of measuring $\Delta\phi(\Theta)$, we can measure $\Delta G(\Theta)$. The obtained estimates are also of interest for the physics of the Schottky barrier: in the paper [11] it is shown that the presence of an extremum for the function $\Delta\phi(\Theta)$ (for a certain value of $\Theta^*$) indicates pinning of the Fermi level at the metal–semiconductor contact.

### Conflict of interest

The authors declare that they have no conflict of interest.

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