Adsorption of Barium Atoms on Silicon Carbide

S. Yu. Davydov[a]* and O. V. Posrednik[b]

[a] *Ioffe Physical Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia*
[b] *St. Petersburg Electrotechnical University LETI, St. Petersburg, 197376 Russia*
*e-mail: Sergei_Davydov@mail.ru

Abstract—The adsorption of barium atoms on C and Si faces of $3C$-, $6H$-, and $4H$-SiC polytypes is examined using the Haldane−Anderson model. The charge transfer from a barium adatom to the substrate is analyzed with band and local states of the adsorption system taken into account. The ionic and metallic contributions to the adsorption energy are estimated. The surface molecule model is used to verify some of the results.

Keywords: band and local states, charge transfer, ionic and metallic components of the adsorption energy.

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Numerous polytypes of silicon carbide, which are wide-band-gap semiconductors characterized by high temperature, mechanical, and radiation resistance, hold much promise as materials for various device structures [1−4]. More recently, they were used as substrates for graphene layers [5]. Although silicon carbide is used widely, its adsorption properties remain understudied. We published our first model description of adsorption of atoms and molecules on SiC with low degrees of coverage (when an adparticle may be considered isolated) in [6, 7]. In the present study, the adsorption of barium atoms on C and Si faces of SiC polytypes is considered. The interest in this adsorption system stems largely from the results presented in [8], where the Ba/SiC/Si(111)-8° heterostructure was examined experimentally and the formation of a new carbon nanostructure was demonstrated.

The model approach to adsorption was detailed in [9, 10]. It should be noted that a free barium atom has two electrons on the outer s shell with the intraatomic Coulomb repulsion acting between them. Since only one electron "contributes" to the adatom−substrate charge transfer, the problem may be reduced to a single-electron one (by analogy with [11], where the adsorption of vanadium on rutile was studied). The adatom state density then takes the following form:

$$\rho_a(\omega) = \frac{1}{\pi} \frac{\Gamma(\omega)}{[\omega - \varepsilon_a - \Lambda(\omega)]^2 + \Gamma^2(\omega)}. \quad (1)$$

Here, ω is an energy variable; ε_a is the adparticle single-electron level energy; $\Gamma(\omega) = \pi V^2 \rho_{\mathrm{sub}}(\omega)$ is the broadening function of the adparticle quasi-level, where $\rho_{\mathrm{sub}}(\omega)$ is the density of states of the substrate and V is the matrix

element of the adparticle−substrate interaction; and $\Lambda(\omega) = V^2 \int_{-\infty}^{\infty} \rho_{\mathrm{sub}}(\omega')(\omega - \omega')^{-1} d\omega'$ is the quasi-level shift function. The simple Haldane−Anderson model [6, 7, 9, 10] is convenient for characterizing the density of states of the semiconductor substrate. In this model, $\rho_{\mathrm{sub}}(\omega) = \rho_s$ for $|\omega - E_0| \geq E_g/2$ and $\rho_{\mathrm{sub}}(\omega) = 0$ for $|\omega - E_0| < E_g/2$, where $E_0 = \chi + E_g/2$ is the energy of the band-gap center relative to vacuum (taken as the reference point) and χ is the electron affinity of a SiC polytype [12]. Then, $\Gamma \equiv \pi V^2 \rho_s = \mathrm{const}$ and $\Lambda(\omega) = (\Gamma/\pi)\ln|(\omega - E_g/2)/(\omega + E_g/2)|$.

The adatom quasi-level energy measured relative to the band-gap center of silicon carbide is $\varepsilon_a = -I + e^2/4d + E_0$, where $I = 5.21$ eV [13] is the Ba atom ionization energy, d is the adsorption bond length, and e is the electron charge [6, 7, 9, 10]. Since the atomic radii of barium and carbon are 2.24 and 0.77 Å [13], $d = r_a(\mathrm{Ba}) + r_a(\mathrm{C}) = 3.01$ Å for adsorption on the C face; in the case of adsorption on the Si face, $d = r_a(\mathrm{Ba}) + r_a(\mathrm{Si}) = 3.42$ Å, since $r_a(\mathrm{Si}) = 1.18$ Å [13]. The energy parameters for $3C$-, $6H$-, and $4H$-SiC polytypes and the values of ε_a are listed in Table 1.

Adparticle occupation number n_a is the sum of band n_v and local n_l contributions [6, 7, 9, 10]. It was demonstrated in [9] that valence-band contribution n_v may be calculated using the following approximate formula:

$$n_v = \frac{1}{\pi} \mathrm{arccot}\frac{\varepsilon_a + R}{\Gamma}, \quad R = \frac{E_g}{2}\sqrt{1 + \frac{4\Gamma}{\pi E_g}}. \quad (2)$$

Adatom quasi-level half-width Γ is typically regarded as a fitting parameter. At $\Gamma = E_g/8$, the values of n_v given in Table 1 are obtained. Let us analyze the effect of Γ on the results.

Local state energy ω_l, where $|\omega_l| < E_g/2$, is determined by solving the $\omega - \varepsilon_a - \Lambda(\omega) = 0$ equation, and the occupation number of this state is

$$n_l = \bar{n}_l \Theta(E_F - \omega_l), \quad \bar{n}_l = \left(1 + \frac{\Gamma}{\pi} \frac{E_g}{(E_g/2)^2 - \omega_l^2}\right)^{-1}, \quad (3)$$

where Heaviside function $\Theta(E_F - \omega_l)$ ensures that only the contributions of levels lying below the Fermi level (E_F) are taken into account [9, 10]. The values of $\bar{n}_l$ are listed in Table 2.

Adsorption energy E_{ads} may be presented as a sum of ionic E_{ads}^{ion} and metallic E_{ads}^{met} components [9, 10]. The ionic component may be estimated as

$$E_{ads}^{ion} = -\frac{(Ze)^2}{4d}, \quad (4)$$

where $Z = 1 - n$ is the adatom charge (or the adatom–substrate charge transfer). The values of E_{ads}^{ion} for unoccupied local levels lying above the Fermi level ($E_{ads}^{ion} >$) and occupied local levels below the Fermi level ($E_{ads}^{ion} <$) are listed in Table 2.

Metallic component E_{ads}^{met} of the adsorption energy may be estimated using the Heisenberg uncertainty relation ($\Delta x \Delta p \sim \hbar$). Assuming that $\Delta x \sim r_a$(Ba) in an isolated atom and $\Delta x \sim d$ in the adsorbed state, we obtain kinetic energy gain $\Delta E_{kin} \sim (\hbar^2/2md^2)[1 - (r_a/d)^2]$, where m is the mass of a free electron. As in [9], it is taken as the simplest order-of-magnitude estimate of the metallic component of the adsorption energy:

$$E_{ads}^{met} = -\frac{\hbar^2}{2md^2}\left(1 - \frac{r_a^2}{d^2}\right). \quad (5)$$

$E_{ads}^{met} = -0.19$ eV is obtained for both faces. It is easy now to determine the values of total adsorption energy E_{ads} (Table 2).

Let us analyze the obtained results. Level ε_a shifts toward the center of the band gap (while remaining in its upper half) in the $3C \to 6H \to 4H$ polytype series. This shift enhances band contribution n_v to occupation number n. Local levels ω_l and their occupation numbers $\bar{n}_l$ in the indicated polytype series behave similarly to ε_a and n_v. The difference is that $n_v \ll 1$, while the value of $\bar{n}_l$ is close to unity. If the Fermi level lies close to the upper edge of the valence band (p-SiC), charge Z of a barium adatom is close to +1; if the Fermi level is near the lower edge of the conduc-

Table 1. Characteristics of the Ba/SiC system: band gap E_g, electron affinity χ, energy ε_a of the barium adatom quasi-level measured relative to the band-gap center, and band contribution n_v to the occupation number (all energy values are given in eV)

Parameter	Polytype		
	3C	6H	4H
E_g	2.40	3.00	3.23
χ	4.00	3.45	3.17
E_0	5.20	4.95	4.785
C face			
ε_a	1.19	0.94	0.77
n_v	0.04	0.05	0.05
Si face			
ε_a	1.04	0.79	0.63
n_v	0.04	0.05	0.05

Table 2. Energy ω_l of the local level and its occupation number $\bar{n}_l$ at $\omega_l < E_F$, ionic component E_{ads}^{ion} of the adsorption energy, and total adsorption energy E_{ads} for the Ba/SiC system ($E_{ads}^{ion} >$ corresponds to $\omega_l > E_F$; $E_{ads}^{ion} <$, to $\omega_l < E_F$). All energy values are given in eV

Parameter	Polytype		
	3C	6H	4H
ω_l			
C face	0.97	0.82	0.68
Si face	0.86	0.69	0.56
$\bar{n}_l$			
C face	0.69	0.83	0.81
Si face	0.75	0.85	0.85
C face			
$-E_{ads}^{ion} >$	0.09	0.02	0.02
$-E_{ads}^{ion} <$	1.10	1.08	1.08
$-E_{ads} >$	0.28	0.21	0.21
$-E_{ads} <$	1.29	1.27	1.27
Si face			
$-E_{ads}^{ion} >$	0.09	0.02	0.02
$-E_{ads}^{ion} <$	0.97	0.95	0.95
$-E_{ads} >$	0.28	0.21	0.21
$-E_{ads} <$	1.16	1.14	1.14

tion band (n-SiC), $Z \sim 0$. Therefore, in the former case, ionic component $E_{ads}^{ion} \sim 1$ eV; i.e., it is approximately five times larger in magnitude than metallic component E_{ads}^{met}. In the latter case, $E_{ads}^{ion} \sim 0$ and $E_{ads} \approx$
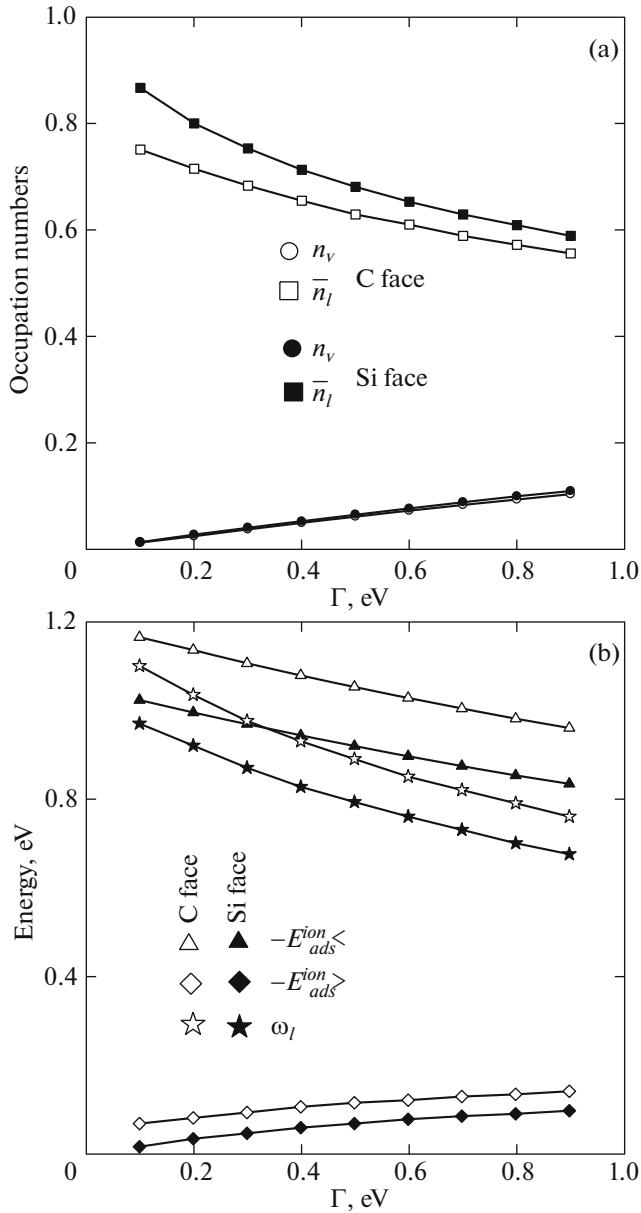
Fig. 1. Adsorption of a barium atom on C and Si faces of polytype $3C$ of silicon carbide. (a) Dependences of band n_v (circles) and local $\bar{n}_l$ (squares) contributions to the total occupation number on adatom quasi-level half-width Γ. (b) Dependences of ionic contributions $-E_{ads}^{ion} <$ (triangles) and $-E_{ads}^{ion} >$ (diamonds; the values are multiplied by 10) with their signs reversed and energy ω_l of the local level (asterisks) on adatom quasi-level half-width Γ. Open and filled symbols correspond to the adsorption on C and Si faces. $E_{ads}^{ion} >$ corresponds to $\omega_l > E_F$; $E_{ads}^{ion} <$, to $\omega_l < E_F$. The energy interval in (b) is coincident with the upper half of the band gap of $3C$-SiC.

E_{ads}^{met}. The dependences of calculated values on the quasi-level half-width are presented in Fig. 1. It can be seen that the contributions to occupation numbers n_v and $\bar{n}_l$ depend monotonically and rather weakly on Γ

(Fig. 1a). The same is true for energies ω_l and E_{ads}^{ion}. Therefore, the relatively arbitrary setting of Γ does not alter the results qualitatively.

An alternative estimate of the charge transfer and the Ba atom−substrate binding energy is obtained using the diatomic surface molecule (BaC, BaSi) model and the Harrison binding-orbital method [14, 15]. Energies $\varepsilon_h = (\varepsilon_s + 3\varepsilon_p)/4$, where ε_s and ε_p are the energies of s and p states, of the sp^3 orbitals of C and Si atoms are $\varepsilon_h(C) = -11.11$ eV and $\varepsilon_h(Si) = -8.28$ eV, since $\varepsilon_s(C) = -17.52$ eV, $\varepsilon_p(C) = -8.97$ eV, $\varepsilon_s(Si) = -13.55$ eV, and $\varepsilon_p(Si) = -6.52$ eV (Herman−Skillman tables of atomic terms [14]). Let us consider the σ bond between the s orbital of a Ba atom and the sp^3 orbital of C and Si atoms. Since $\varepsilon_s(Ba) = -4.45$ eV [14], the polar energies are

$$V_3(Ba-C) = (\varepsilon_h(C) - \varepsilon_s(Ba))/2 = 3.33 \text{ eV},$$

$$V_3(Ba-Si) = (\varepsilon_h(Si) - \varepsilon_s(Ba))/2 = 1.92 \text{ eV}.$$

The covalent binding energy is $V_2 = [(\eta_{ss\sigma} + \eta_{sp\sigma}\sqrt{3})/2](\eta^2/md^2)$ [16], where m is the mass of an electron, $\eta_{ss\sigma} = 1.32$, and $\eta_{sp\sigma} = 1.42$ [15]. Thus, $V_2(Ba-C) = 1.59$ eV and $V_2(Ba-Si) = 1.23$ eV. The bond polarity is defined as $\alpha_p = V_3/\sqrt{V_2^2 + V_3^2}$; therefore, $\alpha_c(Ba-C) = 0.90$ and $\alpha_c(Ba-Si) = 0.84$. Switching to the adsorption problem and assuming $Z = \alpha_p$, we obtain $E_{ads}^{ion}(Ba-C) = -0.97$ eV and $E_{ads}^{ion}(Ba-Si) = -0.74$ eV from (4). These values agree fairly well with the $E_{ads}^{ion} <$ values from Table 2. Thus, two different approaches indicate that the Ba adatom−substrate binding is markedly ionic in the case of p-SiC.

Unfortunately, we were unable to compare the obtained results with experimental data on the energy of Ba adsorption on SiC. In contrast to the adsorption of metals on metals [17], the adsorption of metals on semiconductors is poorly studied, and no data even on the energy of Ba adsorption on silicon and diamond could be found (although certain data on these (or close) adsorption systems are given in [18−21]). Let us, thus, turn to cesium adsorption. First-principles calculations for the Cs/Si(001) system with coverage degree $\Theta = 0.5$ yield adsorption energies for various adsorption positions falling within the range from -1.46 to -2.46 eV [22]. Similar calculations for cesium atoms on graphite yield an adsorption energy of -1.42 eV [23]. This indirect validation of the obtained results is the only one available at present.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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