ISSN 1063-7834, Physics of the Solid State, 2019, Vol. 61, No. 8, pp. 1490–1493. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Fizika Tverdogo Tela, 2019, Vol. 61, No. 8, pp. 1538–1541.

SURFACE PHYSICS AND THIN FILMS

On the Adsorption of Gases on Silicon Carbide: Simple Estimates

S. Yu. Davydov[a], * and O. V. Posrednik[b]
[a] Ioffe Institute, St. Petersburg, 194021 Russia
[b] Saint-Petersburg Electrotechnical University, St. Petersburg, 197376 Russia
* e-mail: Sergei_Davydov@mail.ru

Received March 19, 2019; revised March 19, 2019; accepted April 2, 2019

Abstract—The adsorption of atomic and molecular nitrogen and ammonia on silicon carbide is considered within two physically different (solid-state and quantum-chemical) approaches. In the solid-state approach, the Haldane–Anderson model is used for the density of states of the SiC 4H and 6H polytypes to demonstrate that the energy of binding to the substrate is 6 and 3 eV for N atoms and N_2 molecule, respectively. In the quantum-chemical approach, the model of a surface diatomic molecule is used to find that the binding energy of atomic nitrogen is 6 and 4 eV for adsorption on the C- and Si-edges, respectively. It has been established that the charge transfer between an adsorbate and the substrate may be neglected in all the considered cases. It has been hypothesized that the dissociation of a molecule with the further passivation of its dangling sp^3-orbitals with hydrogen atoms takes place for silicon carbide as in the case of ammonia adsorption on Si(100).

Keywords: Haldane–Anderson model, surface molecule model, charge transfer, adsorption energy

DOI: 10.1134/S1063783419080109

1. INTRODUCTION

Silicon carbide attracts the attention of researchers, first of all, as a wide band-gap material with increased resistance to thermal, mechanical, and radiation impacts, which enables the use of devices based on this material under extremal conditions [1–3]. In the past decade, silicon carbide has found the new field of application as an initial object for the formation of carbon nanostructures [4, 5]. An original method of SiC synthesis from silicon (method of assembly) has also recently been proposed [6]. In light of the aforesaid, the question about the adsorbability of silicon carbide is of interest. In this work, we shall present the theoretical estimates for the charge transfer and the energy of binding with the silicon carbide surface for some atoms and molecules. Let us note that there also exist some model approaches to the problem of adsorption in addition to the popular and currently widely used first-principles calculations (generally, within different density functional variants). Here, the most consistent variant is the approximation based on the Haldane–Anderson model [7–9]. An ideologically close, but simplified approach uses the modified Anderson model [10, 11]. Finally, considering the adsorption in a surface molecule [7], it is possible to find simple estimates using the Harrison method of bonding orbitals [12]. In this work, the first and third approaches are used. N_2, NH_3, and N atoms are considered as adsorbates. Let us note that the problem of interaction between the N_2 and NH_3 gases and the SiC surface has risen when studying the SiO_2/SiC interface [13–17]. In this case, the dissociation of molecules takes place. We have not managed to find any works just on the adsorption of N_2, N, and NH_3 on SiC. For this reason, our given considerations below will be based on indirect data and some assumptions, as it is incorrect to extrapolate the results [13–17] obtained for a volume to the case of a surface.

2. HALDANE–ANDERSON MODEL

2.1. General Relationships

From the general point of view [7–9], the Green function $G_a(\omega)$ for an adsorbed particle (adparticle) can be written as

$$G_a^{-1}(\omega) = \omega - \varepsilon_a - \Lambda_a(\omega) + i\Gamma_a(\omega). \quad (1)$$

Here, ω is the energy variable, ε_a is the energy of the single-electron level of an adparticle, $\Gamma_a(\omega) = \pi V_a^2 \rho_{\text{sub}}(\omega)$ is the adparticle quasi-level broadening function, where $\rho_{\text{sub}}(\omega)$ is the density of states for the substrate, V_a is the matrix adparticle–substrate interaction element, and $\Lambda_a(\omega) = \frac{1}{\pi} P\int_{-\infty}^{\infty} \frac{\Gamma_a(\omega')d\omega'}{\omega - \omega'}$ is the quasi-level shift function, where P is the principal value integral symbol. The density of states (DOS) on an adparticle

$\rho_a(\omega)$ corresponding to the Green function (Eq. (1)) has the form

$$\rho_a(\omega) = \frac{1}{\pi}\frac{\Gamma_a(\omega)}{[\omega - \varepsilon_a - \Lambda_a(\omega)]^2 + \Gamma_a^2(\omega)},$$

and the occupation number n_a of the level ε_a of an adparticle at zero temperature is

$$n_a = \int\limits_{-\infty}^{E_\mathrm{F}} \rho_a(\omega)d\omega, \tag{2}$$

where E_F is the Fermi level of the substrate.

The adsorption energy is $E_\mathrm{ads} = E_\mathrm{ads}^\mathrm{met} + E_\mathrm{sub}^\mathrm{ion}$, where the first summand is the metallic component of the adsorption energy, and the second is the ionic component.

It can be demonstrated [7, 8] that

$$E_\mathrm{ads}^\mathrm{met} = \int\limits_{-\infty}^{E_\mathrm{F}} (\omega - E_\mathrm{F})\Delta\rho_\mathrm{sys}(\omega)d\omega, \tag{3}$$

where $\Delta\rho_\mathrm{sys} = \rho_\mathrm{sys} - \rho_\mathrm{sys}^0$, and ρ_sys^0 and ρ_sys is the system DOS before and after adsorption. The ionic component can be estimated as

$$E_\mathrm{sub}^\mathrm{iot} = -\frac{(Z_a e)^2}{4d}, \tag{4}$$

where Z_a is the adparticle charge equal to $1 - n_a$, if an orbital was initially occupied and $(-n_a)$, if an orbital is empty, and d is the adsorption bond length.

Let us note that hereinafter we consider a single-electron (or single-hole) particle, which can contain a single electron (hole) on its outermost orbital due to intraatomic Coulomb repulsion [7–9].

For the description of a semiconductor substrate, it is very convenient to use the simple Haldane–Anderson model [7–9], in which $\rho_\mathrm{sub}(\omega) = \rho_s$ 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 bandgap center with respect to the vacuum level, and χ is the electron affinity of a silicon carbide polytype. Then $\Gamma_s = \pi V_a^2 \rho_s$ = const, and $\Lambda(\omega) = (\Gamma/\pi)\ln|(\omega - E_0 - E_g/2)/(\omega - E_0 + E_g/2)|$. In this case, in the absence of degeneracy for the semiconductor substrate, the adparticle occupation number $n_a = n_\mathrm{v} + n_l$ [7–9], where the valence band contribution according to Eq. (2) is

$$n_\mathrm{v} = \int\limits_{-\infty}^{-E_g/2} \rho_a(\omega)d\omega, \tag{5}$$

and the local state contribution is

$$n_l = \left(1 + \frac{1}{\pi}\frac{\Gamma_s E_g}{(E_g/2)^2 - \omega_l^2}\right)^{-1} \Theta(E_\mathrm{F} - \varepsilon_l), \tag{6}$$

where ω_l is the energy of a local state laying within the bandgap and is the root of the equation $\omega - \varepsilon_a - \Lambda_a(\omega) = 0$ within a range $|\omega| < E_g/2$, and $\Theta(...)$ is the Heaviside function.

2.2. Adsorption of an N_2 Molecule

Let us consider the adsorption of an N_2 molecule on SiC. According to [18], the electron affinity χ and the bandgap width E_g for the SiC 4H and 6H polytypes are 3.17, 3.23 eV and 3.45, 3.00 eV, respectively. Hereinafter, zero energy is taken to be the position of the bandgap center with respect to the vacuum level: $E_0 = \chi + E_g/2$. The ionization energy of an N_2 molecule is $I = 15.58$ eV [19]. The quasi-level energy is $\varepsilon_a = -I + e^2/4d + E_0$, where the second summand describes the Coulomb shift of the quasi-level of an adparticle [7, 8]. Assuming that $d = 1$ Å (approximately equal to the interatomic distance in an N_2 molecule [20]), we obtain $\varepsilon_a = -7.20$ eV (4H–SiC) and $\varepsilon_a = -7.03$ eV (6H–SiC). It is clear that such deep seated levels contain a single electron, so an admolecule almost has no charge, and the ionic component (Eq. (4)) of the adsorption energy $E_\mathrm{ads}^\mathrm{ion} \sim 0$.

Indeed, let us estimate the valence band contributions n_v (Eq. (5)) to the occupation numbers n_a by the formula for (see [9]) as

$$n_\mathrm{v} = \frac{1}{\pi}\mathrm{arccot}\frac{\varepsilon_a + R}{\Gamma_s}, \quad R = \frac{E_g}{2}\sqrt{1 + \frac{4\Gamma_s}{\pi E_g}}. \tag{7}$$

At $\Gamma_s = 0.5$ eV, we obtain from Eqs. (7) that $n_\mathrm{v} \sim 1$ for both 4H–SiC and 6H–SiC. On the other hand, $n_l \sim 0$ (see Eq. (6) and Fig. 1 in [9]), so $n_a \sim 1$, and $Z_a \sim 0$.

To estimate the metallic (or covalent) component of the adsorption energy $E_\mathrm{ads}^\mathrm{met}$ (Eq. (3)), let us use the uncertainty relation $\Delta x \Delta p \sim \hbar$. Assuming that $\Delta x \sim d$ in an isolated molecule, and $\Delta x \sim 2d$ in an adsorbed state, we obtain the kinetic energy gain $\Delta E_\mathrm{kin} \sim 3\hbar^2/8md^2 \approx 3\ \mathrm{eV} \sim \left|E_\mathrm{ads}^\mathrm{met}\right|$, where m is the mass of a free electron.

Let us note that, when the Haldane–Anderson model is used, the distinctions in adsorption on Si- and C-edges are taken into account only through the matrix element V_a and, therefore, Γ_s. If it is assumed within the solid-state approach that the adsorption bond lengths for Si- and C-edges are the same, these distinctions completely disappear (see, however, Section 2.3 below).

As already mentioned, unfortunately, we have not managed to find any literature data on the adsorption energy of an N_2 molecule on SiC. According to the data [21], an N_2 molecule does not dissociate on W(110). We also assumed in the given estimates that just a molecule is adsorbed on SiC rather than nitrogen atoms.

2.3. Adsorption of an NH_3 Molecule and an N Atom

In the adsorption of NH_3 molecules on Si(100), the dissociation of a molecule takes place [21]. Thus formed hydrogen atoms passivate the dangling sp^3-orbitals of silicon, thereby stopping the reaction. There are no grounds to believe that this is not the case on the Si- and C-edges of silicon carbide. Hence, no adsorption of molecular ammonia occurs on silicon carbide.

Let us now consider the adsorption of atomic nitrogen on silicon carbide. The ionization energy of a nitrogen atom is $I = 14.53$ eV [19], which slightly differ from the ionization energy of an N_2 molecule. Assuming again that $d = 1$ Å (approximately equal to the interatomic distance in an N_2 molecule [20]), we obtain $\varepsilon_a = -6.15$ eV (4H–SiC) and $\varepsilon_a = -5.98$ eV (6H–SiC). Similarly to the case of N_2/SiC, they correspond to deep-seated levels, so the transfer of charge may be neglected. Hence, the ionic component of the adsorption energy is $E_{\text{ads}}^{\text{ion}} \sim 0$. For the kinetic energy gain, we newly have the expression $\Delta E_{\text{kin}} \sim 3\hbar^2/8md^2$, where d may be set equal to the atomic radius of nitrogen $r_N = 0.71$ Å. Then we obtain that $\Delta E_{\text{kin}} \sim 6 \text{ eV} \sim \left|E_{\text{ads}}^{\text{met}}\right|$.

3. METHOD OF BONDING ORBITALS

The considered approach to the adsorption problem from the previous section may be called the solid-state approach equivalent to the problem on an impurity in a solid-state matrix. In this section, we use the quantum-chemical approximation, within which a cluster composed of an adsorbed particle and its nearest substrate atoms is considered. In the limiting case, such a cluster can be reduced to a diatomic molecule composed of an adatom, which is directly bonded to a substrate atom (the model of a surface molecule) [7].

Let us begin with the consideration of the adsorption of a nitrogen atom on the C-face of SiC. Within the method of bonding orbitals (MBO) [12], we obtain the C–N bond length $d_{\text{CN}} = r_N + r_C = 1.48$ Å, where the atomic radius of carbon is $r_C = 0.77$ Å [19]. For the σ-bond of the carbon sp^3-orbital with the nitrogen p-orbital, the covalent bond energy is $V_2 = (\hbar^2/md_{\text{CN}}^2)(\eta_{sp\sigma} + \sqrt{3}\eta_{pp\sigma})/2$ [22], where $\eta_{sp\sigma} = 1.42$, and $\eta = 2.22$ [12, 23], whence we obtain that $V_2(\text{CN}) = 0.16$ eV. The energy of the hybrid carbon sp^3-orbital is $-\varepsilon_h(\text{C}) = (\varepsilon_s + 3\varepsilon_p)/4 = 13.15$ eV, and the energy of the nitrogen p-orbital is $s_p = -13.84$ eV (tables of Mann atomic terms [12, 24]). Whence the polar energy of the C–N bond is determined as $V_3(\text{CN}) = (\varepsilon_h(\text{C}) - \varepsilon_p(\text{N}))/2 = 0.35$ eV. Then the bond covalency is $\alpha_c = V_2/\sqrt{V_2^2 + V_3^2} \approx 1$. The bond energy can be written in the simplest form as

$$E_b \approx \frac{2V_2}{\alpha_c}\left(1 - \frac{2}{3}\alpha_c^2\right)$$

(see, e.g., Eq. (3) in the work [25] where, however, we have changed the sign of E_b), whence we find that $E_b(\text{CN}) \approx 2V_2/3 \approx 6$ eV. Let us note that we assume in this model that $E_b = -E_{\text{ads}}$, so the value found by us for $E_b(\text{CN})$ coincides with the result of Section 2. The same takes place for the transfer of charge, which is estimated within MBO by the bond polarity $\alpha_P = \sqrt{1 - \alpha_c^2} \ll 1$.

Let us now turn to the adsorption of nitrogen atoms on the Si-face of SiC. Since $r_{\text{Si}} = 1.18$ Å, we have $d_{\text{SiN}} = r_N + r_{\text{Si}} = 1.89$ Å, and $V_2(\text{SiN}) = 5.62$ eV. Since $-\varepsilon_h(\text{Si}) = (\varepsilon_s + 3\varepsilon_p)/4 = 9.39$ eV, we obtain $V_3(\text{SiN}) = (\varepsilon_h(\text{Si}) - \varepsilon_p(\text{N}))/2 = 2.23$ eV, $\alpha_c \approx 0.97$, and $E_b(\text{SiN}) \approx 4$ eV. Hence, the bond energy of a nitrogen atom on the C-face is one and a half times higher than on the Si-face. In both cases, the bond is almost homopolar.

4. CONCLUSIONS

Hence, the charge transfer between an adparticle and the SiC substrate and the adsorption energy were estimated in this work using two principally different models: (1) the solid-state model, which explicitly takes into account the existence of the substrate bandgap, but ignores the nature of an face of adsorption (C or Si) and the geometry of an adsorbed complex and (2) the model of a surface molecule, where the band energy structure of the substrate is not taken into account at all, but the difference between the adsorption bond lengths on the C- and Si-faces is taken into consideration. The comparison of the results obtained by different models shows their good agreement with each other. In addition to nearly equal adsorption energy values, it is worth mentioning the coincidence of estimates for the nearly zero charge transfer between the adsorbate and the adsorbent. It is of interest to note that the charge transfer in the adsorption of gases on d metals is also extremely small [26]. It should also be emphasized that both simple approximations used here can rather easily be modified for the specific features of the adsorption system to be more strictly taken into account (see, e.g., [27, 28]).

ACKNOWLEDGMENTS

The authors are grateful to S.A. Kukushkin for proposing the topic and useful discussions.

CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

REFERENCES

1. *Silicon Carbide: Recent Major Advances*, Ed. by W. J. Choyke, H. Matsunami, and G. Pensl (Springer, Berlin, Heidelberg, 2004). http://www.springer.de.
2. *Advances in Silicon Carbide. Processing and Applications*, Ed. by S. E. Saddow and A. Agarwal (Artech House, Boston, London, 2004). www.artechhouse.com.
3. A. A. Lebedev, Semicond. Sci. Technol. **21**, R17 (2006).
4. Y. H. Woo, T. Yu, and Z. X. Chen, Appl. Phys. Rev. **108**, 071301 (2010).
5. G. V. Benemanskaya, P. A. Dement'ev, S. A. Kukushkin, A. V. Osipov, and S. N. Timoshnev, Tech. Phys. Lett. **45**, 201 (2019).
6. S. A. Kukushkin, A. V. Osipov, and N. A. Feoktistov, Phys. Solid State **56**, 1507 (2014).
7. S. Yu. Davydov, *Adsorption Theory: Model Hamiltonian Method* (SPbGETU LETI, St. Petersburg, 2013) [in Russian]; twirpx.com/file/1596114/.
8. S. Yu. Davydov, A. A. Lebedev, and O. V. Posrednik, *An Elementary Introduction to the Theory of Nanosystems* (Lan', St. Petersburg, 2014) [in Russian].
9. S. Yu. Davydov and S. V. Troshin, Phys. Solid State **49**, 1583 (2007).
10. S. Yu. Davydov and A. V. Pavlyk, Semiconductors **35**, 796 (2001).
11. S. Yu. Davydov and A. V. Pavlyk, Tech. Phys. Lett. **29**, 500 (2003).
12. S. Yu. Davydov and O. V. Posrednik, *The Method of Bonding Orbitals in Semiconductor Theory, the School-Book* (SPbGETU LETI, St. Petersburg, 2007) [in Russian]; twirpx.com/file/1014608/.
13. J. P. Xu, P. T. Lai, C. L. Chan, and Y. C. Cheng, Appl. Phys. Lett. **76**, 372 (2000).
14. Y. S. Liu, S. Hashimoto, K. Abe, R. Hayashibe, T. Yamakami, M. Nakao, and K. Kamimura, Jpn. J. Appl. Phys. **44**, 673 (2005).
15. Y. Iwasaki, H. Yano, T. Hatayama, Y. Uraoka, and T. Fuyuki, Appl. Phys. Express **3**, 026201 (2010).
16. F. Liu, C. Carraro, A. P. Pisano, and R. Maboudian, J. Micromech. Microeng. **20**, 035011 (2010).
17. E. Pitthan, A. L. Gobbi, H. I. Boudinov, and F. C. Stedile, J. Electron. Mater. **44**, 2823 (2009).
18. C. Yu. Davydov, Semiconductors **53**, 699 (2019).
19. *Physical Values, The Handbook*, Ed. by E. S. Grigor'ev and E. Z. Meilikhov (Energoatomizdat, Moscow, 1991) [in Russian].
20. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Ed. by L. E. Sutton (The Chemical Society, London, 1958).
21. M. D. Ramsier and J. T. Yates, Jr., Surf. Sci. Rep. **12**, 243 (1991).
22. S. Yu. Davydov and S. K. Tikhonov, Phys. Solid State **37**, 1514 (1995).
23. W. A. Harrison, Phys. Rev. B **27**, 3552 (1983).
24. W. A. Harrison, Phys. Rev. B **31**, 2121 (1985).
25. S. Yu. Davydov and O. V. Posrednik, Phys. Solid State **57**, 837 (2015).
26. L. A. Bol'shov, A. P. Napartovich, A. G. Naumovets, and A. G. Fedorus, Sov. Phys. Usp. **20**, 432 (1977).
27. S. Yu. Davydov, Tech. Phys. **59**, 624 (2014).
28. S. Yu. Davydov, A. V. Zubov, and A. A. Lebedev, Tech. Phys. Lett. **45** (5) (2019, in press).

Translated by E. Glushachenkova