

# Initial Stages of Metal Films Growth on a SiO<sub>2</sub>-Cristobalite Surface

V.G. Zavodinsky<sup>1,2,\*</sup> and A.P. Kuz'menko<sup>2</sup>

<sup>1</sup>*Institute for Materials Science of the Russian Academy of Sciences, Khabarovsk, 680042, Russia*

<sup>2</sup>*South West State University, 305040, Kursk, Russia*

**Abstract:** Using the density functional theory approach and pseudopotentials we studied energetics and electron structures of metal layers (Al, Cu, Ni, and Cr) deposited on a cristobalite surface. We have found that the properties of the first adsorbed layers decide by interaction of metal atoms with oxygen atoms of a substrate surface. Aluminum as an easily oxidized metal, is characterized by the high adhesion, it is followed by nickel and chromium, and copper closes the studied group of metals. Further plating is characterized by significant reduction of binding energy; the properties of films tend to properties of bulk metals.

**Keywords:** Film growth, adsorption energy, metals, quartz, modeling, PACS 62.20.Mk.

## 1. INTRODUCTION

The metal films deposited by various methods on dielectric substrates are traditional elements of many electronic devices. Their properties in many respects depend both on a way of deposition and on nature and structure of a substrate. Though the main features of films growth are described rather well [1-3], thin details of these features, which act at the first steps of growing, remain studied not enough and demand a research at the atomic level. One of the essential moments of this problem is that growth of films of various metals happens miscellaneously even on the same substrate.

For example, Cooley *et al.* [4] noted that aluminum does not follow the mechanism of epitaxial growth on WSe<sub>2</sub> crystal surface, unlike such metals as Au, Ag, Cu, Pd and Co. Authors explain this effect with the fact that aluminum forms strong chemical bonds with selenium and becomes immobile on this substrate. Another example of the aluminum behavior during the films growth process was described by Llusca *et al.* [5] who have written that the interaction of aluminum with SiO<sub>2</sub> surface leads to formation of the Al<sub>2</sub>O<sub>3</sub> interlayer. Satoa *et al.* [6] studied growth of films of copper and aluminum on a surface of SiO<sub>2</sub>; they have shown that recrystallization of aluminum films requires much bigger time and temperature of annealing than it is required for copper films. On the other hand, Ino *et al.* [7] have noted that, on the NaCl surface all studied by them, metals (Ni, Cu, Ag, Au, Al) successfully formed epitaxial films.

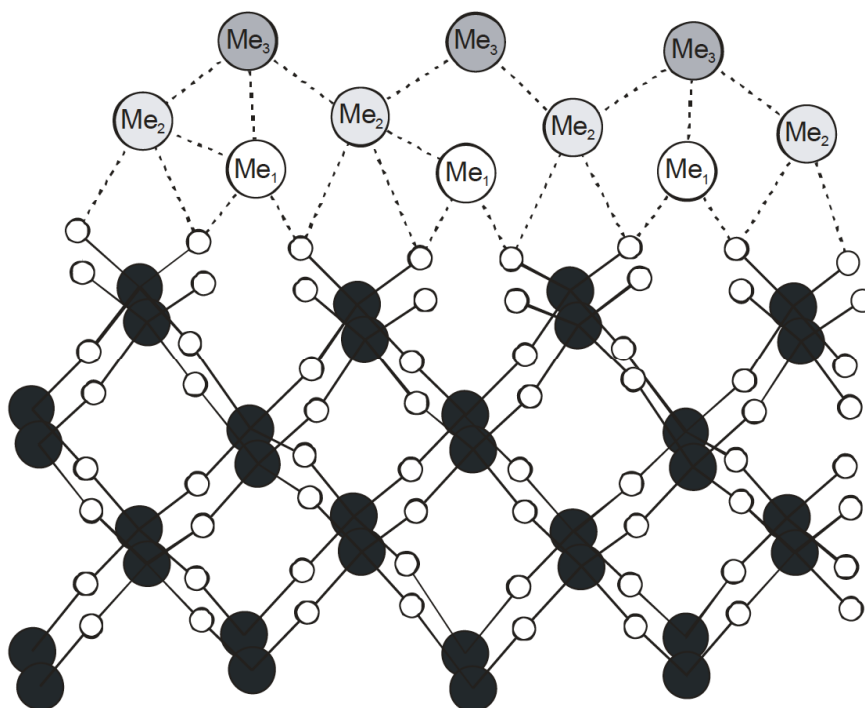
It is known that features of behavior of aluminum on oxide substrates (in particular on SiO<sub>2</sub> surface) are qualitatively connected with its tendency to form steady Al<sub>2</sub>O<sub>3</sub> compound [8-10]. However quantitative data on interaction of Al atoms with SiO<sub>2</sub> are not enough. Our work is devoted to the comparative theoretical study of structure, energy and electronic states of Al, Cu, Ni and Cr films at the initial growth stage on the surface of crystalline quartz (cristobalite). Cristobalite was chosen as the simplest crystal form of quartz that is convenient for modeling.

## 2. METHOD AND TECHNIQUE

A slab of cristobalite used by us for studying of Al, Cu, Ni, and Cr depositions is presented in Figure 1. The slab contains four layers of silicon and four layers of oxygen in the direction of Z. Black spheres in this Figure are silicon atoms, small white spheres are oxygen atoms, big white spheres are the metal atoms participating in the first stage of adsorption (Me<sub>1</sub>), light-gray spheres are atoms of the second stage of adsorption (Me<sub>2</sub>), dark gray spheres are atoms of the third stage of adsorption (Me<sub>3</sub>). The ratio of Si and O amounts corresponds to SiO<sub>2</sub> stoichiometry. The slab periodically repeats at the XY plane that corresponds to modeling of an infinite plate, which surface may be considered as a surface of an infinite crystal. The lower surface of the slab is terminated by silicon atoms. However in reality such surface would be instantly oxidized in the air atmosphere. Therefore we investigated adsorption of metal atoms only on the upper surface terminated by oxygen.

Thus, each atom of the first stage of adsorption (Me<sub>1</sub>) is bonded with two atoms of oxygen, each of which is bonded with one atom of silicon; an atom of the second stage of adsorption (Me<sub>2</sub>) is bonded with

Address correspondence to this article at the Institute for Materials Science of the Russian Academy of Sciences, Khabarovsk, 680042, Russia; Tel: +74212226956; Fax: +74212226598; E-mail: vzavod@mail.ru



**Figure 1:** The schematic image of a slab of cristobalite with indication of positions for consecutive adsorption of metal atoms.

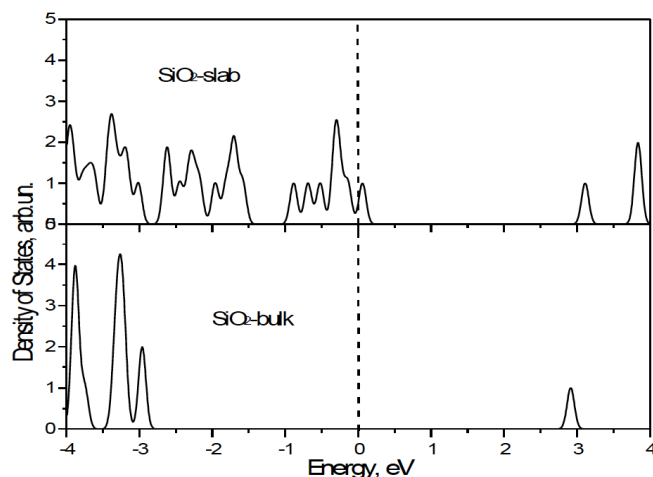
two atoms of oxygen, each of which is bonded with one atom of silicon and with one atom (Me<sub>1</sub>); an atom of the third stage of adsorption (Me<sub>3</sub>) is bonded with one atom (Me<sub>1</sub>) and two atoms (Me<sub>2</sub>).

Simulation of behavior of metal atoms on the cristobalite surface was carried out within the density functional theory [11, 12] and the pseudopotential approach [13]. The FHI96spin code [14] was used for finding of equilibrium structures, total energies, electronic structures and spin polarizations. Pseudopotentials were constructed using the FHI98PP package [15] and were tested on the absence of ghost states. Exchange-correlation interaction was calculated within generalized gradient approximation [16]. The plane wave energy cutoff was taken 40 Ry. All calculations were carried out with use of one k-point ( $\gamma$  point). Silicon atoms of the lower surface of a cristobalite slab were fixed, but all other atoms of the studied system had the chance to move under the influence of interatomic forces and to find their equilibrium positions.

### 3. RESULTS AND DISCUSSION

The electronic structure of the bulk cristobalite (SiO<sub>2</sub>-bulk) and plate (SiO<sub>2</sub>-slab) is presented in Figure 2. We see that bulk cristobalite is a dielectric with the energy gap of about 6 eV, but its electronic spectrum has empty states situated nearby of occupied states

and correspond to nonsaturated bonds of surface oxygen atoms.



**Figure 2:** Density of electronic states of SiO<sub>2</sub>-cristobalite. A vertical dashed line displays the position of the Fermi level.

Calculations consisted of several stages. At the preparatory stage we found an equilibrium configuration and total energy of a slab without putting metal atoms on it. At the same stage we calculated energies of single atoms  $E_{at}$  (Me), Me = Al, Cu, Ni, and Cr. It turned out that an Al atom had no spin polarization at all and that a Cu atom had a very small magnetic moment ( $0.0005 \mu_B$ ) while Ni and Cr atoms had big magnetic moments ( $2.0$  and  $4.0 \mu_B$ ). The pure cristobalite slab did not show any spin polarization.

The bridge positions  $Me_1$ , which are shown in Figure 1 were found as the most favorable positions for metal atoms at the first adsorption step for all studied elements. Energy of this adsorption  $E_{ad1}$  was calculated using the formula

$$E_{ad1} = \frac{E(\text{sub} + Me_1) - E(\text{sub}) - N_1 \cdot E_{at}(Me)}{N_1}, \quad (1)$$

where  $E(\text{sub})$  is the substrate energy;  $E(\text{sub} + Me_1)$  is the energy of the system consisted of the pure substrate and metal atoms  $Me_1$  adsorbed at the pure substrate;  $N_1$  is the number of metal atoms of the first ad-layer. Results of calculations are given in Table 1 in comparison to data on the atom-atom interactions of these metals with oxygen,  $E_{bond}(Me-O)$  [17-20].

**Table 1: The First-Layer Adsorption energies  $E_{ad1}$  and Energies of Atom-Atom Interactions  $E_{bond}(Me-O)$ .**

	Al	Cu	Ni	Cr
$E_{ad1}$ , eV/atom	10.6	5.5	7.5	7.4
$E_{bond}(Me-O)$ , eV	5.3	3.6	4.1	4.4

From Table 1 it is clear that aluminum is characterized by the maximal energy of the first adsorbed atoms; and the minimal energy corresponds to copper. These results correlate with the known data

on the energy of interaction of these metals with oxygen.

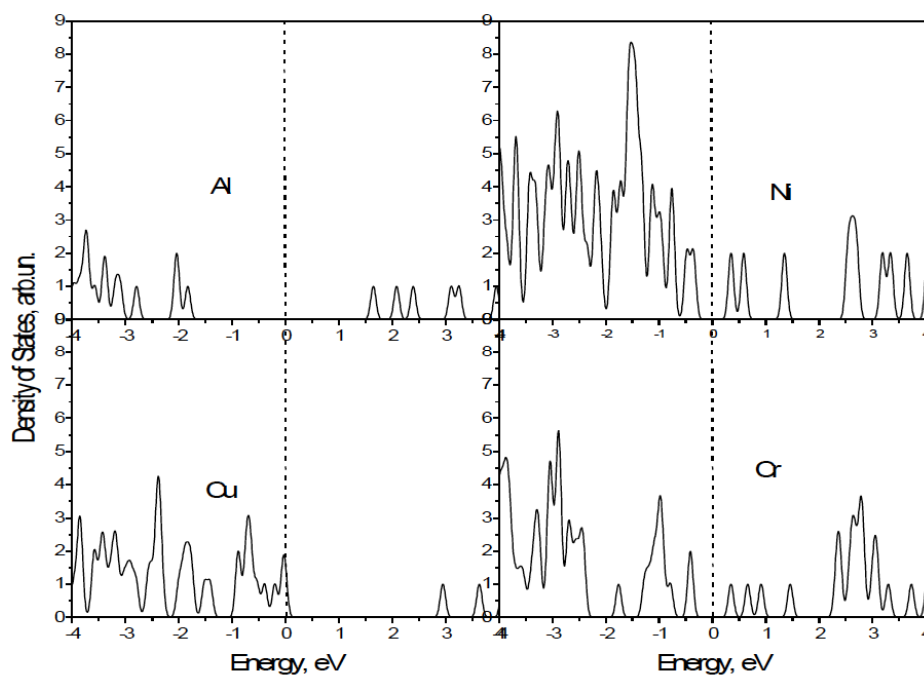
The electronic structure corresponding to deposition of the first atoms of metals on a surface of the cristobalite is presented in Figure 3.

The analysis of Figure 3 shows that aluminum atoms, each of which possesses three valence electrons, quite successfully saturate oxygen bonds therefore the total electronic spectrum of the  $SiO_2$ -Al system gains dielectric character with the energy gap of about 3 eV. Atoms of copper are monovalent ones; they are not able to saturate oxygen bonds, and as a result there is nonzero density of states at the level of Fermi. Atoms of nickel and chrome saturate oxygen bonds; however these atoms have excess quantity of valence electrons which lead to formation of new surface states.

Metal atoms of the second adsorption layer also contact oxygen atoms (see Figure 1). Energy of this adsorption of  $E_{ad2}$  was calculated using the formula

$$E_{ad2} = \frac{E(\text{sub} + Me_1 + Me_2) - E(\text{sub} + Me_1) - N_2 \cdot E_{at}(Me)}{N_2}, \quad (2)$$

where  $E(\text{sub} + Me_1 + Me_2)$  is the energy of the system consisted of the pure substrate, the metal atoms  $Me_1$  and  $Me_2$ ;  $N_2$  is the number of metal atoms of the



**Figure 3:** Density of electronic states of the  $SiO_2$ -cristobalite, on the surface of which the first layer of metal atoms ( $Me_1$ ) is adsorbed.

second ad-layer. Other terms are the same as in Eq. 1. Results of calculations are given in Table 2.

**Table 2: The Second-Layer Adsorption Energies  $E_{ad2}$**

	Al	Cu	Ni	Cr
$E_{ad2}$ , eV/atom	2.7	3.4	3.5	2.2

From Table 2 we see that values of  $E_{ad2}$  are significantly less than the corresponding values of  $E_{ad1}$ . In this case, copper and nickel become leaders. The electronic structures corresponding to deposition of the second atomic layers of Al, Cu, Ni and Cr metals on the cristobalite surface are presented in Figure 4. It is visible that electronic spectra of the SiO<sub>2</sub>-Cu, SiO<sub>2</sub>-Ni, and SiO<sub>2</sub>-Cr systems begin to gain metallic features and the dielectric gap in the SiO<sub>2</sub>-Al system considerably decreases: from 3 to 1 eV.

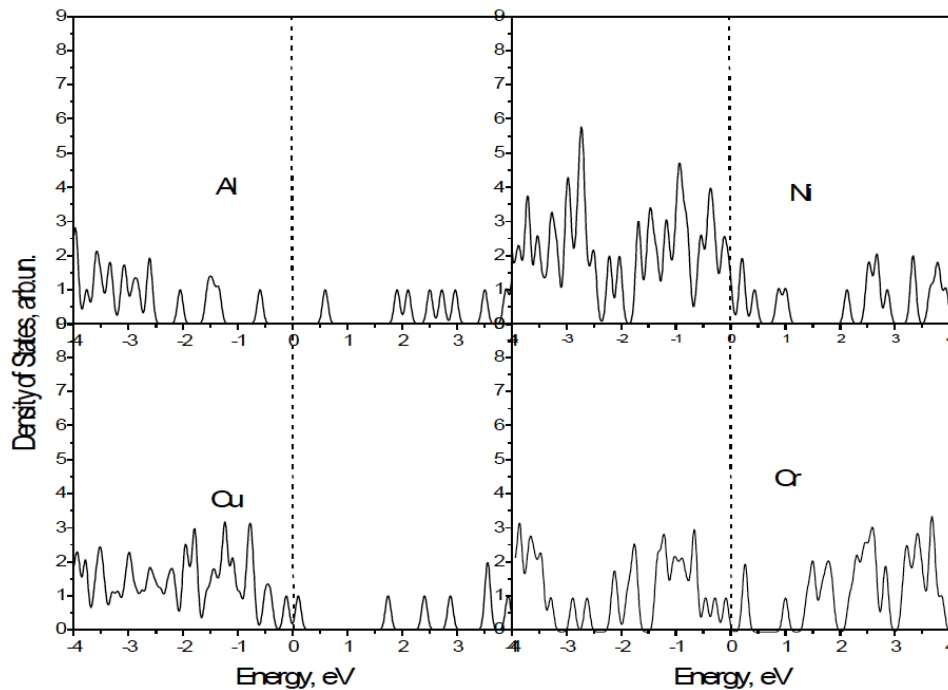
Deposition of the third metal layer ( $Me_3$ ) is characterized by the fact that all surface atoms of

oxygen are already bonded with metal atoms ( $Me_1$  and  $Me_2$ ) and with silicon, thus additional atoms can contact only metal atoms  $Me_2$ . Results of calculations of energy for the third adsorption layer ( $Me_3$ ) are given in Table 3 in comparison to cohesion energy of bulk metals [21]. From Table 3 we see that at this growth step the adsorption energy becomes closer to the cohesion energy of bulk metals.

The electronic structures corresponding to deposition of the third atomic layers of Al, Cu, Ni and Cr metals on the cristobalite surface are presented in Figure 5. From this Figure it is possible to see that in this case the tendency to formation of metal properties is even more amplified than in previous case: namely, the Cu, Ni, and Cr cases demonstrate nonzero densities of states near the Fermi level; the Al spectrum becomes more metallic.

#### 4. CONCLUSIONS

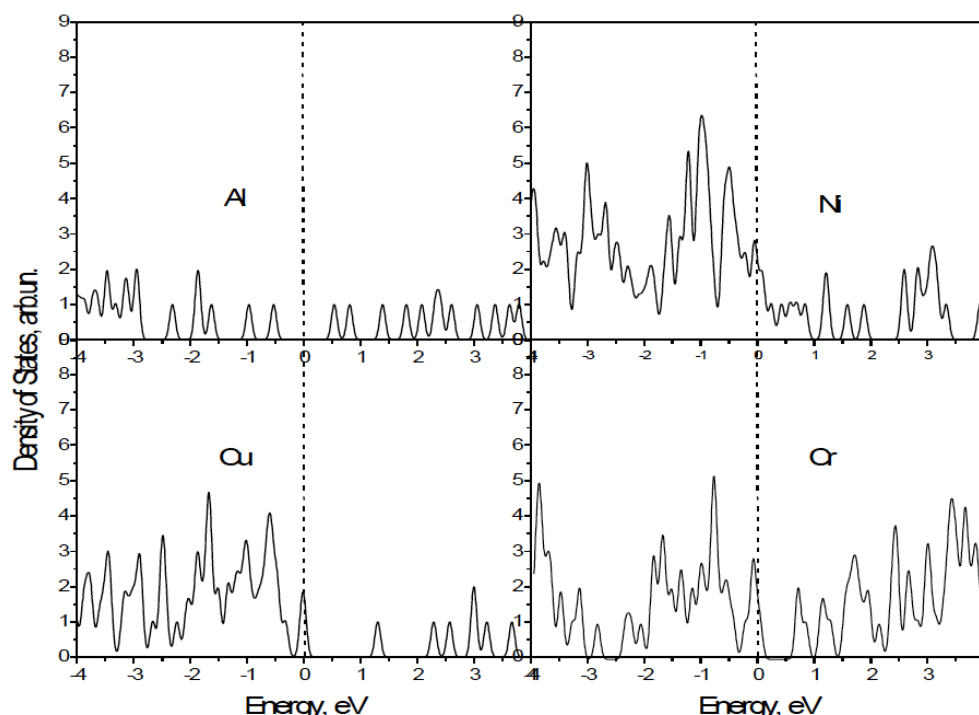
Quantum-mechanical calculations show that the bonding energetics of metal layers deposited on the



**Figure 4:** Density of electronic states of the SiO<sub>2</sub>-cristobalite, on the surface of which the second layer of metal atoms ( $Me_2$ ) is adsorbed.

**Table 3: The Third-Layer Adsorption Energies  $E_{ad3}$  and the Cohesive Metal Bulk Energies**

	Al	Cu	Ni	Cr
$E_{ad3}$ , eV/atom	2.8	3.5	3.6	3.4
$E_{coh}$ , eV/atom	3.39	3.49	4.44	4.10



**Figure 5:** Density of electronic states of the SiO<sub>2</sub>-cristobalite, on the surface of which the third layer of metal atoms (Me<sub>3</sub>) is adsorbed.

cristobalite substrate first of all depends on the nature of interaction of these metals with oxygen. Aluminum as easily oxidized metal is characterized by high adhesion per atom (10.6 eV). It is followed by nickel and chromium (respectively 7.5 and 7.4 eV) and copper closes the studied group of metals (5.5 eV). This stage may be called chemical adsorption. Further plating is characterized by physical adsorption with significant reduction of binding energy; growth of films tends the properties to those of bulk metals that demonstrate both the gradual increase in binding energies and formation of metal nature of the electronic spectra.

## REFERENCES

- [1] Marcia H. Grabow and George H. Gilmer. Thin film growth modes, wetting and cluster nucleation. *Surf Sci* 1988; 94: 333-346. [https://doi.org/10.1016/0039-6028\(88\)90858-8](https://doi.org/10.1016/0039-6028(88)90858-8)
- [2] Kaiser N. Review of the fundamentals of thin-film growth. *Applied Optics* 2002; 41(16): 3053-3060. <https://doi.org/10.1364/AO.41.003053>
- [3] Stavale F. Fundamental aspects on thin film growth. [http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching\\_wintersemester\\_2012\\_2013/fern\\_ando\\_stavale\\_thinfilm\\_growth\\_121130.pdf](http://www.fhi-berlin.mpg.de/acnew/department/pages/teaching/pages/teaching_wintersemester_2012_2013/fern_ando_stavale_thinfilm_growth_121130.pdf).
- [4] Cooley KA, Alsaadi R, Gurunathan RL, Domask AC, Kerstetter L, Saidib WA, Mohnya SE. Room-temperature epitaxy of metal thin films on tungsten diselenide. *J Crystal Growth* 2019; 505: 44-51. <https://doi.org/10.1016/j.jcrysgro.2018.09.040>
- [5] Llusca M, Antony A, Bertomeu J. Growth and properties of ZnO:Al on textured glass for thin film solar cells. *Int J Photoenergy* 2014; ID 406495. <https://doi.org/10.1155/2014/406495>
- [6] Satoa Y, Suzuki T, Mogami H, Otake F, Hatori H, Igarashi S. Solid phase growth of some metal and metal oxide thin films on sapphire and quartz glass substrates. *Materials Sci Forum* 2013; 753: 505-509. <https://doi.org/10.4028/www.scientific.net/MSF.753.505>
- [7] Ino S, Watanabe D, Ogawa S. Epitaxial growth of metals on rocksalt faces cleaved in vacuum. *J Phys Soc Japan* 1964; 19(6): 881-891. <https://doi.org/10.1143/JPSJ.19.881>
- [8] Roberts S, Dobson PJ. Evidence for reaction at the Al-SiO<sub>2</sub> interface. *J Phys D: Appl Phys* 1981; 14: L17-22. <https://doi.org/10.1088/0022-3727/14/3/001>
- [9] Zhu H, Dong K, Huang J, Li J, Wang G, Xie Z. Reaction mechanism and mechanical properties of an aluminum-based composite fabricated in-situ from Al-SiO<sub>2</sub> system. *Materials Chem Phys* 2014; 145: 334-341. <https://doi.org/10.1016/j.matchemphys.2014.02.020>
- [10] Bauer RS, Bachrach RZ, Brillson LJ. Au and Al interface reactions with SiO<sub>2</sub>. *Appl Phys Lett* 1980; 37: 1006-1008. <https://doi.org/10.1063/1.91720>
- [11] Hohenberg H, Kohn W. Inhomogeneous electron gas. *Phys Rev* 1964; 136: B864-B871. <https://doi.org/10.1103/PhysRev.136.B864>
- [12] Kohn W, Sham JL. Self-consistent equations including exchange and correlation effects. *Phys Rev* 1965; 140: A1133-A1138. <https://doi.org/10.1103/PhysRev.140.A1133>
- [13] Cohen ML, Heine V. Pseudopotential theory of cohesion and structure. In: Ehrenreich H, Seitz F, Turnbull D, editors. *Solid State Physics*, New York: Academic Press 1970; 24: 38-249. [https://doi.org/10.1016/S0081-1947\(08\)60071-5](https://doi.org/10.1016/S0081-1947(08)60071-5)
- [14] Beckstedte M, Kley A, Neugebauer J, Scheffler M. Density functional theory calculations for poly-atomic systems: electronic structure, static and elastic properties and ab initio

- molecular dynamic. Comput Phys Commun 1997; 107: 187-205.  
[https://doi.org/10.1016/S0010-4655\(97\)00117-3](https://doi.org/10.1016/S0010-4655(97)00117-3)
- [15] Fuchs M, Scheffler M. Ab initio pseudopotentials for electronic structure calculations of poly-atomic systems using density functional theory. Comput Phys Commun 1999; 119: 67-165.  
[https://doi.org/10.1016/S0010-4655\(98\)00201-X](https://doi.org/10.1016/S0010-4655(98)00201-X)
- [16] Perdew JP, Wang Y. Accurate and simple density functional for the electronic exchange energy. Phys Rev B 1986; 33: 8800-8802.  
<https://doi.org/10.1103/PhysRevB.33.8800>
- [17] Cottrell TL. The Strengths of Chemical Bonds, 2d ed., Butterworth, London 1958.
- [18] De B, Darwent B. National Standard Reference Data Series, National Bureau of Standards, No. 31, Washington 1970.
- [19] Benson SW. Bond energies. J Chem Educ 1965; 42(9): 502-518.  
<https://doi.org/10.1021/ed042p502>
- [20] Kerr JA. Bond dissociation energies by kinetic methods. Chem Rev 1966; 66(5): 465-500.  
<https://doi.org/10.1021/cr60243a001>
- [21] Kittel Ch. Introduction to Solid State Physics, 8<sup>th</sup> edition. Hoboken, NJ: John Wiley & Sons, Inc, 2005.

---

Received on 03-09-2019

Accepted on 20-09-2019

Published on 26-09-2019

[DOI: https://doi.org/10.31875/2410-4701.2019.06.3](https://doi.org/10.31875/2410-4701.2019.06.3)

© 2019 Zavodinsky and Kuz'menko; Zeal Press

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.