First-principle modeling of gold adsorption on BeO (0001)

S. Barzilai [*],[1], F. Tavazza, L.E. Levine

Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8553, Gaithersburg, MD 20899, USA

ARTICLE INFO

ABSTRACT

Gold nanowire chains are considered a good candidate for nanoelectronic devices since they exhibit remarkable structural and electrical properties. For practical engineering devices, α-wurtzite BeO may be a useful platform for supporting these nanowires, since the atom separation of the BeO (0001) surface is compatible with the Au–Au atom spacing. However, its influence on the nanowire conductivity is unknown. Here, ab initio simulations of adsorption of one gold atom on cleaved BeO (0001) surfaces have been performed to find the most favorable adsorption site. An attractive adsorption was obtained for all the studied sites, but the most favorable site was above the oxygen for the O-terminated surface and above the Be–Be bridge for the Be-terminated surface. A relatively high electron density is observed in the Au–O and Au–Be bonds, and the local density of states exhibits high peaks in the vicinity of the Fermi energy.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Gold nanowires have attracted a great deal of attention since they exhibit remarkable electrical and structural properties which make them candidates for applied areas such as nanoelectronic devices. Many experimental [1–10] and theoretical [11–24] studies have been carried out to explain these properties, however only a few studies [25–28] attempt to characterize them when the nanowires are placed atop a suitable substrate that is needed for practical engineering devices. Those studies investigate the transport properties of gold chains on a metallic NiAl(110) substrate which is useful for conductive, straight, single atom chains but may prove to be inadequate for more complicated chain configurations such as two dimensional (2D) zigzag or hexagonal structures [24] due to its surface symmetry, or for nanoscale circuits which include resistors and semiconductors made from these nanowires due to its conductivity.

α-Wurtzite BeO may be a useful platform for supporting such nanoscale gold chains. This compound has a band gap of 10.6 eV [29], high thermal conductivity [30], sixfold symmetry on the basal plane and bond lengths which are similar to the Au–Au bond length in low-energy nanoscale configurations. Moreover, BeO has good corrosion and a thermal-shock resistance.

As a first step toward characterizing the conductance of several configurations of gold nanowires lying atop a BeO (0001) surface, it is necessary to investigate the interaction between a gold atom and the BeO surface to find the favorable adsorption sites and to characterize the nature of their bonding. This understanding is also important for numerous applications, such as coating, brazing, soldering,

catalysis and fabrication of composite materials where earth alkali oxides, and especially BeO, may be involved.

The preferential adsorption of metallic elements at the substrate surface can be predicted by ab initio analysis using density functional theory (DFT) methods. Earlier calculations have considered such calculations for several types of metallic atoms adsorbed onto CaF_2 [31–33]. The present study is limited to the adsorption calculation of a single Au atom on a BeO (0001) surface, while computations of adsorption and conductance of several gold atoms in a nanowire structure will be pursued in future studies.

Results are presented for ab-initio calculations of a Au atom placed above three different sites on both oxygen- and beryllium-terminated BeO (0001) surfaces. The adsorption potential (i.e., the interaction energy) is computed for each site and for different metal–surface distances. At the equilibrium distance, the adsorption energy and various properties of the electronic structure are presented to elucidate the nature of the bonding. These results suggest that gold nanowires on BeO (0001) may be a suitable system for building nano-devices and justify pursuing a more exhaustive conductance study.

2. Methodology

Cluster (non-periodic boundary conditions) calculations were performed assuming an ideal condition of 0 K, with surfaces free of contamination and defects. The calculations were carried out in the framework of DFT, using the DMol[3] code [34–36]. We used a real space cut-off of 4.0 Å and a double-numeric basis set with polarization functions (DND). The exchange-correlation potential was treated within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [37]. The ion core electrons of the Au were described by a hardness conserving semi-local pseudopotential (DSPP) [38] and only the outer electrons ($5s^2 5p^6 5d^{10} 6s^1$) were treated as

* Corresponding author. Tel.: +1 3019758359.
  E-mail address: barzilai.shmuel@gmail.com (S. Barzilai).
[1] On sabbatical leave from the Nuclear Research Center NEGEV.

valence electrons. Several calculations were made with unrestricted spin polarization and only a minute effect was observed. Thus, to save computational time, we performed restricted spin polarization to all of the calculations described here. To ensure that the results of the calculations are directly comparable, identical conditions were employed for all systems. The convergence criteria for the energy calculation and structure optimization were: 1.6×10^{-4} eV (6×10^{-6} Ha) for self-consistent calculations, 10^{-4} Å for maximum displacement and 1.4×10^{-3} eV (5×10^{-5} Ha) for energy change.

The hexagonal BeO wurtzite structure can be described as alternating parallel beryllium and oxygen layers perpendicular to the c axis. Cutting the crystal perpendicular to this axis creates a Be-terminated (0001) surface on one side of the cut and an O-terminated surface on the other side of the cut. For each surface, we considered three different adsorption sites as described in Section 3. We used a relatively large substrate with non-periodic boundary conditions to explore the effect of a single adsorbate on the near and far neighbors, to minimize the side effect of the substrate on the adsorption potential and to investigate the magnitude of the atomic configuration changes at the edges of the substrate. This substrate has six layers and 24 or 25 atoms on each layer (Fig. 1). The adsorption potentials were calculated for a Au atom above a non-relaxed substrate having bulk bond lengths, and above a substrate that was relaxed previously. For the latter, the atoms of the two bottom layers of the substrate were kept fixed during the relaxation, while the rest of the atoms were allowed to relax. To examine the stability of the Au atoms in their selected sites, further relaxations were made, allowing the Au adsorbate to move on the surface, and the surface to relax due to the interaction with the adsorbate. The results from these calculations revealed the preferred configurations of Au on the surface. For these configurations, the electron density and the density of states (DOS) were computed.

To compute DOS results, it is necessary to use periodic boundary conditions. Here, we used a super-cell of 10 Å × 17 Å to have continuity in the XY directions and a top vacuum layer of 15 Å. For this calculation, one k-point sampling was incorporated using the Monkhorst–Pack scheme [39]. It should be recalled that DFT calculations provide access to the DOS of the non-interacting Kohn–Sham reference system, rather than that of the fully interacting system of electrons [40], but the two systems may be expected to be qualitatively similar. The relaxation was performed by the conjugate gradient approach based on a delocalized internal coordinate scheme [41,42].

To estimate size effects of substrate thickness, three oxygen-terminated surfaces having thicknesses of 6, 8 and 10 layers were relaxed and representative adsorption calculations were made (Eq. (1)) for Au above the central oxygen of each. To reduce the computational expense for the substrate relaxation, only nine atoms were used for each substrate layer. It was found that the thickness of the relaxed

substrate has only a small effect on the adsorption energy. For a substrate containing 8 and 10 layers, the adsorption energy difference was less than 0.05 eV compared to the energy calculated for substrates containing 6 layers, used in our standard calculations. As the effect of adding more layers beyond 10 should be much smaller, we can claim that the inaccuracy of our results caused by the finite substrate thickness is ≈50 meV. Similar effects of substrate thickness were obtained previously for Au on MgO (001) [43]. In this case, the adsorption energy exhibits only minor changes (less than 30 meV) for substrates containing 2 or more layers. Comparing this rock-salt structure to the relaxed BeO (0001) structure, these 2 layers may be equivalent to 4 layers in the wurtzite structure. In both cases, these layers represent two couples of Me–O (Me = Be or Mg).

3. Results and discussion

The calculations were performed for Au adsorbed on oxygen- and beryllium-terminated surfaces of BeO (0001) (Fig. 1). For each surface, three adsorption sites were considered (a) atop the oxygen, (b) atop the beryllium and (c) atop the bridge triplet (BT) formed by the top-most atoms of the surface. In each case, the adsorption energy, the electron density and the DOS of the adsorbed Au were studied.

3.1. Adsorption energy

The total energies of the BeO (0001)/Au systems were calculated for the sites shown in Fig. 1, for distances of 1.4 Å to 9.0 Å between the Au and the terminate layer of each surface. The adsorption potential (U_{ads}) was calculated according to:

$$U_{ads}(z) = E_{tot}^{sys}(z) - \left(E_{tot}^{substrate} + E_{tot}^{Au} \right), \tag{1}$$

where $E_{tot}^{sys}(z)$ is the total energy of the substrate with Au atom, calculated for each adsorption site at various distances (z) from the substrate surface. For the non-relaxed surface, this baseline was fixed, whereas for the relaxed substrate, the average location of the top most atomic layer is used as the base line. $E_{tot}^{substrate}$ is the total energy of the substrate configuration without the Au atom, and E_{tot}^{Au} refers to the total energy of the single Au without the substrate. For Au that is well-separated from the BeO substrates, the condition $\lim_{z \to 0} U_{ads}(z) = 0$ is satisfied.

To determine an optimal value for the adsorption energy, E_{ads}, it is useful to interpolate the computed results for the adsorption potential. In order to obtain an accurate interpolation, especially in the vicinity of the minimum, we apply Morse-type functions (Eq. (2)) for the cases where both attractive and repulsive interactions were observed in the adsorption potential curves:

$$U = E_{ads} \cdot \left[e^{-2a(z-z^0)} - 2e^{-b(z-z^0)} \right]. \tag{2}$$

Here, E_{ads} represents the adsorption energy, z^0 represents the equilibrium distance, and a and b are constants to be retrieved by fitting the functions to the computed results.

Fig. 2 exhibits the adsorption potential curves of BeO/Au for the three different sites and four types of BeO (0001) surfaces. Table 1 gives the interaction parameters of the fitted functions for each configuration.

As can be seen from the adsorption potential, in all the cases, the gold atom interacts with the substrate in an attractive manner. However, the adsorption energy depends strongly on the nature of the surface. For the non-relaxed surfaces, high adsorption energies (2.8 eV to 4.4 eV) were computed and the BT site was identified as the most favorable adsorption site for both the oxygen- and the beryllium-terminated surface. For the more physically correct relaxed surfaces, the adsorption energies are much lower (0.58 eV to 0.72 eV)
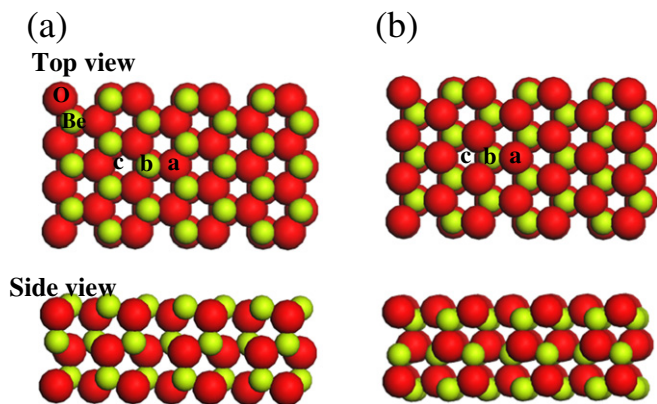

(a) (b)

Top view

Side view

Fig. 1. Top and side view of the sites on BeO (0001) surfaces considered for adsorption; (a) beryllium terminated surface and (b) oxygen terminated surface. The labels a, b, and c, stand for the oxygen, beryllium and BT positions of the Au adsorbate, respectively.
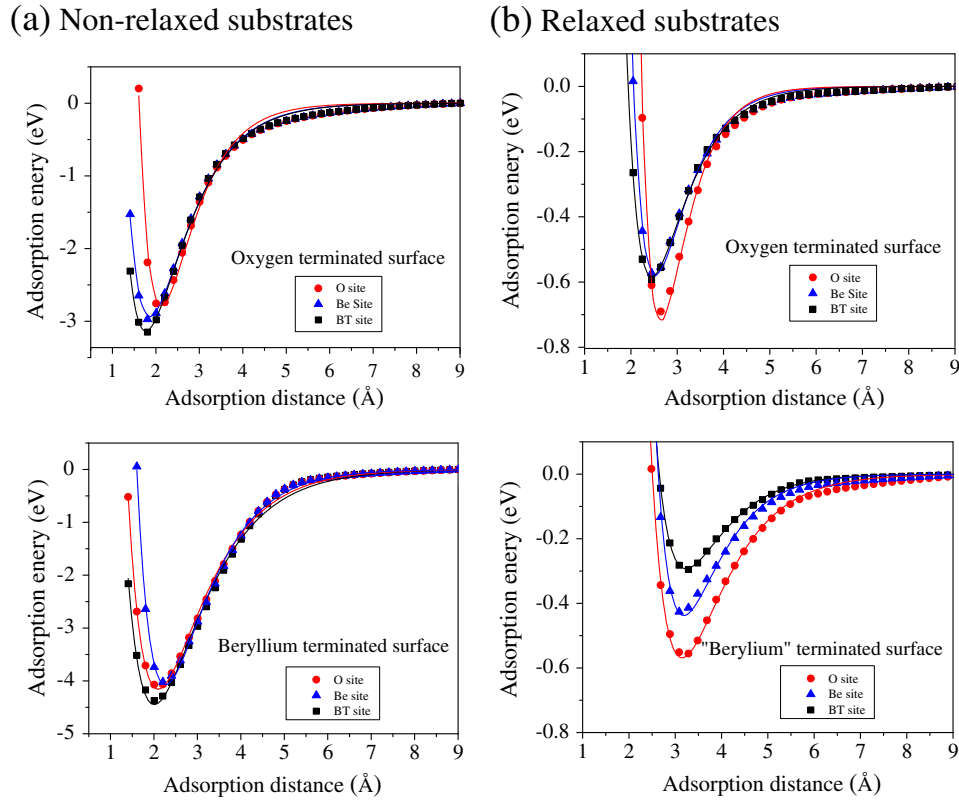
(a) Non-relaxed substrates   (b) Relaxed substrates

Fig. 2. Adsorption potentials of Au atom above oxygen- and beryllium-terminated BeO (0001) surfaces. The adsorption potential was computed for non-relaxed (a) and relaxed (b) substrates. In each figure, the distance is relative to the surface layer. During the relaxation of the Be-terminated surface, the O atoms moved to locations that were slightly above the Be atom positions, thus becoming the top most layer.

and the energetically preferred adsorption site was changed to the O site for both surfaces. Electrostatic considerations [44,45] show that the charge separation that occurs when a polar sample is cleaved leads to an energetically highly-unstable situation. Thus, during the relaxation, the BeO (0001) surfaces may exhibit massive surface reconstructions which can decrease their reactivity. Indeed, during the substrate relaxation, the Be and O atoms moved to overcome this instability. For the oxygen terminated surface, the average distance between the Be and O layers changed from 0.535 Å to 0.28 Å for the top

two layers and to 0.21 Å for the next two layers. Significant changes were also observed for the beryllium-terminated surface. Initially, the beryllium layer was 0.535 Å above the oxygen layer, while after the relaxation, this separation decreased to ≈ -0.04 Å, with the average relaxed O positions slightly higher than that of the Be atoms. These configuration changes may explain the differences between the adsorption energies computed for the relaxed and non-relaxed surfaces.

Further relaxations were carried out to allow the Au adsorbate to move on the surface, and the surface to relax due to the interaction with the adsorbate. For the oxygen-terminated surface, the favorable adsorption site remains above the oxygen, but the Au atom moved ≈ 0.3 Å toward the Be atom. For the beryllium-terminated surface, the Au atom moved to a new adsorption site which is directly above the Be–Be bridge. For both cases, the presence of the gold adsorbate also caused small changes in the positions of the nearby beryllium and oxygen atoms. For these fully relaxed sites, the adsorption energy was computed as 1.2 eV and 1.9 eV for the oxygen- and beryllium-terminated surfaces, respectively. To elucidate the nature of the adsorption bonding and the effect of the substrate relaxation, we examined the electronic structure. This analysis was focused on the most favorable cases that were obtained from the relaxed BeO/Au systems.

3.2. Electronic structure

A deeper understanding of the bonding interaction in the BeO (0001)/Au systems can be achieved by studying their electronic structure. As described previously, the most stable adsorption sites obtained from these relaxed systems were atop the oxygen and above the Be–Be bridge for the O-terminated and Be-terminated

Table 1
Parameters that characterize the adsorption potential of Au atom above oxygen and beryllium terminated of BeO (0001) surfaces, for the relaxed and non-relaxed substrates.

BeO (0001) surface type	Adsorption site	Interaction parameters from Eq. (2)		
		E_{ads}, eV	a, Å^{-1}	z^0, Å
Non-relaxed surface	Be terminated	O	4.16	0.96	2.09
		Be	4.07	1.05	2.26
		BT	4.45	0.92	2.01
	O terminated	O	2.80	1.36	2.12
		Be	2.94	1.16	1.86
		BT	3.14	1.13	1.77
Relaxed surface	Be terminated	O	0.57	1.08	3.15
		Be	0.44	1.26	3.18
		BT	0.29	1.20	3.23
	O terminated	O	0.72	1.73	2.64
		Be	0.58	1.49	2.52
		BT	0.58	1.36	2.45

surfaces, respectively. The redistribution of electrons due to Au adsorption and the local DOS (the DOS of the specified atom, LDOS) near the Fermi energy (E_F) were calculated and related to the tendency of the Au atom to interact with the BeO substrate. Fig. 3a and b shows the electronic structure associated with Au adsorption on the O-terminated surface and Fig. 3c and d shows the same information for the Be-terminated surface.

As can be seen from the electronic structures, for Au adsorbed on the O-terminated surface (Fig. 3a and b), the adsorption bonding of Au can be related to the interaction with a single oxygen atom from the BeO surface. The LDOS indicate that the adsorption hardly affects the electronic structure of the Be atoms, but affects the electronic structure of the Au atom and the oxygen atom adjacent to it. Orbital projected DOS and integrated DOS analyses indicate that the *6s* state of the Au becomes almost empty (see the Au DOS Fig. 3b) with part of the Au charge transferred to the surface and mostly to the *2p* states of the oxygen beneath it. Moreover, the electrons that occupied the *5d* states of Au interact with the *2p* states of O (see electron energies 2 eV to 5 eV below the Fermi energy). A different situation was obtained for the Au adsorption on the Be-terminated surface (Fig. 3c and d). In this case, almost no charge transfer was observed and the adsorption bonding of Au is associated with the interaction with two beryllium atoms and one oxygen atom from the BeO surface. According to the DOS computations (Fig. 3d), this bonding primarily affects the electrons lying in the band that crosses the Fermi energy. Here, a new band is raised for the Be and O atoms beneath the Au. This band does not exist for the Be and O atoms that

are far from the adsorbate and it is associated with the occupied *s* states in Au, *p* states in O and *s,p* states in Be. This triple bonding is consistent with the high adsorption energy observed for this surface.

4. Conclusion

Adsorption of Au on a hexagonal BeO (0001) wurtzite structure was investigated to find the most favorable adsorption sites on the O- and Be-terminated surfaces, and to explore the nature of the interaction. For the adsorption configurations studied, it was found that the relaxation has a major effect on the adsorption energy and on the positions of the substrate atoms close to the surface. After substrate relaxation, the O site was found to be preferred for both Be- and O-terminated surfaces (Fig 2b). Further relaxation, which allowed both the Au adsorbate to move on the surface and the surface to relax due to the interaction with the adsorbate, indicates that the most favorable adsorption site for the Be-terminated surface is located above the Be–Be bridge and for the O-terminated surface it remains above the O. The electronic study shows that, for the Be-terminated surface, the Au atom interacts mainly with two Be atoms and one O atom located beneath it. For the O-terminated surface, the adsorption primarily affects the electronic structure of the O beneath the Au atom. Thus, for future conductance simulations of gold nanowires lying on a BeO surface, it is recommended to place the Au atoms above the O atoms for the O-terminated surface, and above the Be–Be bridge for the Be-terminated surface.
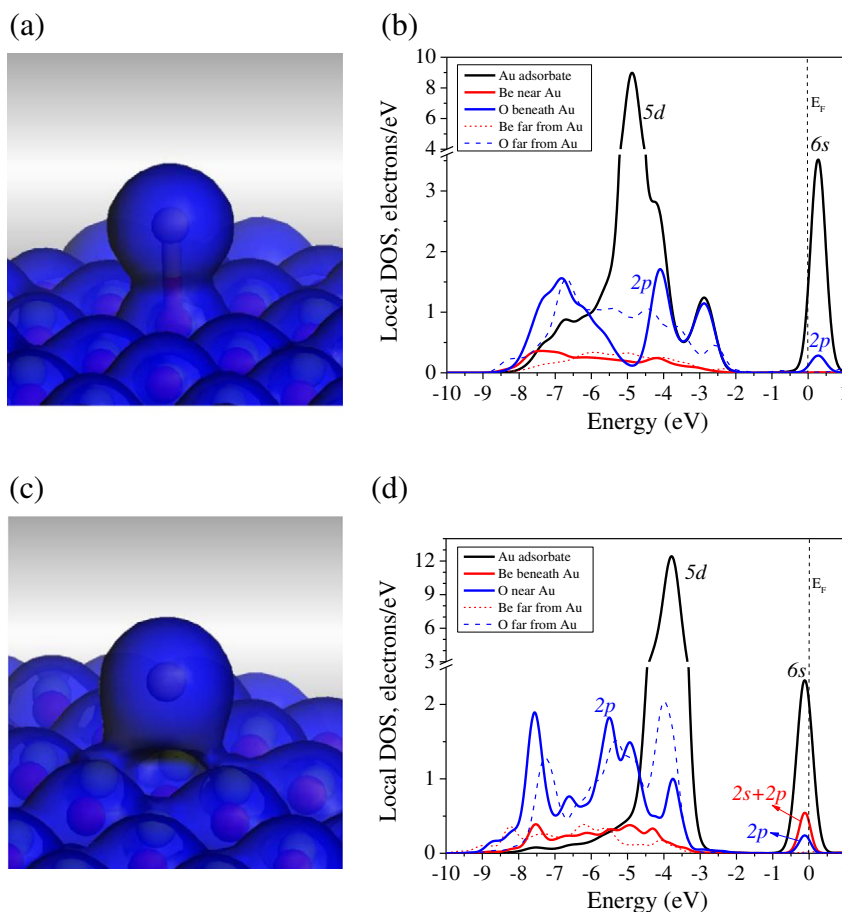

Fig. 3. Electronic structure of the relaxed BeO (0001)/Au systems. (a) and (b) are the electron density iso-surface and the LDOS of the O-terminated/Au system, respectively. (c) and (d) are the electron density iso-surface and the LDOS of the Be-terminated/Au system, respectively. For both systems, the Au atom is placed at the equilibrium adsorption site, and the electron density iso-surfaces correspond to 0.2 e/Å³. The orbitals that dominate the bands are shown.

References

[1] I.K. Yanson, O.I. Shklyarevskii, S. Csonka, H. van Kempen, S. Speller, A.I. Yanso, J.M. van Ruitenbeek, Phys. Rev. Lett. 95 (2005) 256806.
[2] M. Kiguchi, T. Konishi, K. Murakoshi, Phys. Rev. B 73 (2006) 125406.
[3] R. Suzuki, M. Tsutsui, D. Miura, S. Kurokawa, A. Sakai, Jpn. J. Appl. Phys. 46 (2007) 3694.
[4] T. Kizuka, Phys. Rev. B 77 (2008) 155401.
[5] Y. Oshima, Y. Kurui, K. Takayanagi, J. Phys. Soc. Jpn. 79 (2010) 054702.
[6] E. Scheer, et al., Nature 394 (1998) 154.
[7] Y. Kurui, Y. Oshima, M. Okamoto, K. Takayanagi, Phys. Rev. B 79 (2009) 165414.
[8] R.H.M. Smit, C. Untiedt, G. Rubio-Bollinger, R.C. Segers, J.M. van Ruitenbeek, Phys. Rev. Lett. 91 (2003) 076805.
[9] M. Dreher, F. Pauly, J. Heurich, J.C. Cuevas, E. Scheer, P. Nielaba, Phys. Rev. B 72 (2005) 75435.
[10] H. Ohnishi, Y. Kondo, K. Takayanagi, Nature 395 (1998) 780.
[11] F. Tavazza, L.E. Levine, A.M. Chaka, J. Appl. Phys. 106 (2009) 43522.
[12] N. Agraït, A.L. Yeyati, J.M. van Ruitenbeek, Phys. Rep. 377 (2003) 81.
[13] N. Agraït, G. Rubio, S. Vieira, Phys. Rev. Lett. 74 (1995) 3995.
[14] G. Rubio-Bollinger, P. Joyez, N. Agraït, Phys. Rev. Lett. 93 (2004) 11680.
[15] A. Nitzan, M.A. Ratner, Science 300 (2003) 1384.
[16] Z. Qian, R. Li, S. Hou, Z. Xue, S. Sanvito, J. Chem. Phys. 127 (2007) 194710.
[17] M. Brandbyge, J.L. Mozoz, P. Ordejon, J. Taylor, K. Stokbro, Phys. Rev. B 65 (2002) 165401.
[18] Y. Fujimoto, K. Hirose, Phys. Rev. B 67 (2003) 195315.
[19] Y.J. Lee, et al., Phys. Rev. B 69 (2004) 125409.
[20] M. Zhuang, M.J. Ernzerhof, Chem. Phys. 120 (2004) 4921.
[21] A. Grigoriev, et al., Phys. Rev. Lett. 97 (2006) 236807.
[22] L. Ke, et al., Nanotechnology 18 (2007) 095709.
[23] A. Grigoriev, N.V. Skorodumova, S.I. Simak, G. Wendin, B. Johansson, R. Ahuja, Phys. Rev. Lett. 97 (2010) 236807.
[24] F. Tavazza, L.E. Levine, A.M. Chaka, Phys. Rev. B 81 (2010) 235424.
[25] N. Nilius, T.M. Wallis, M. Ho, Science 297 (2002) 1853.
[26] N. Nilius, T.M. Wallis, M. Ho, Appl. Phys. Rev. A 80 (2005) 951.
[27] N. Nilius, T.M. Wallis, M. Persson, M. Ho, Phys. Rev. Lett. 90 (2003) 196103.
[28] A. Calzolari, C. Cavazzoni, M.B. Nardelli, Phys. Rev. Lett. 93 (2004) 96404.
[29] V.A. Sashin, M.A. Bolorizadeh, A.S. Kheifets, M.J. Ford, J. Phys. Condens. Matter 15 (2003) 3567.
[30] G.A. SLACK, J. Phys. Chem. Solids 34 (1973) 321.
[31] S. Barzilai, N. Argaman, N. Froumin, D. Fuks, N. Frage, Surf. Sci. 603 (2009) 2096.
[32] S. Barzilai, N. Argaman, N. Froumin, D. Fuks, N. Frage, Surf. Sci. 602 (2008) 1517.
[33] S. Barzilai, N. Argaman, N. Froumin, D. Fuks, N. Frage, Mater. Sci. Eng., A 495 (2008) 36.
[34] Commercial software is identified to specific procedures. Such identification does not imply recommendation by the National Institute of Standards and Technology.
[35] B. Delley, J. Chem. Phys. 92 (1990) 508.
[36] B. Delley, J. Chem. Phys. 113 (2000) 7756.
[37] J.P. Perdew, S. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[38] B. Delley, J. Phys. Rev. B 66 (2002) 155125.
[39] H.J. Monkhorst, D. Pack, J. Phys. Rev. B 13 (1976) 5188.
[40] G.D. Mahan, Comments Condens. Matter. Phys. 16 (1994) 333.
[41] P. Pulay, G. Fogarasi, J. Chem. Phys. 96 (1992) 2856.
[42] J. Baker, A. Kessi, B. Delley, J. Chem. Phys. 05 (1996) 192.
[43] G. Pacchioni, L. Giordano, M. Baistrocchi, Phys. Rev. Lett. 94 (2005) 226104.
[44] P.W. Tasker, J. Phys. C 12 (1979) 4977.
[45] C. Noguera, J. Phys. Condens. Matter 12 (2000) R367.