PHYSICAL REVIEW B **70**, 165319 (2004)

$SrTiO_3/Si(001)$ epitaxial interface: A density functional theory study

I. N. Yakovkin[1,2] and M. Gutowski[1,3,*]

[1]*Chemical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352, USA*

[2]*Institute of Physics of National Academy of Sciences of Ukraine, Prospect Nauki 46, Kiev, 03028 Ukraine*

[3]*Department of Chemistry, University of Gdansk, 80-952 Gdansk, Poland*

(Received 4 November 2003; revised manuscript received 17 February 2004; published 26 October 2004)

The Sr and SrO monolayers on Si(001) and the $SrTiO_3/Si(001)$ interface have been simulated by means of total energy minimization within the density functional theory formalism and the generalized gradient approximation form of exchange-correlation potential. It has been found that the first SrO layer restores a 1×1 structure of the substrate thus providing a template for subsequent epitaxy of the $SrTiO_3$ layers. The calculated densities of states are in good agreement with recent x-ray and ultraviolet photoemission valence band spectra. The role of the "buffer layer" in forming the electronic structure is discussed and illustrated with an example of SrO monolayer at the $SrTiO_3/Si(001)$ interface.

DOI: 10.1103/PhysRevB.70.165319 PACS number(s): 68.35.Bs, 68.35.Ct, 71.15.Mb

I. INTRODUCTION

Metal oxides are famous for diversity of special dielectric and magnetic properties, which makes them very promising materials for development of new electronic devices. In particular, the high dielectric constant and electron spin polarization of perovskites, like $SrTiO_3$, make them attractive for further development of tunneling semiconductor valves and magnetic tunnel junctions for spintronics applications.[1–6]

However, there are many problems to be solved on the way to maintaining such devices. First, properties of thin films do not necessarily have to reproduce those of bulk materials.[2,3] Second, epitaxial growth of these films on surfaces of routine semiconductor materials, such as silicon, presents a serious challenge.[7–17] For example, TiO_2 crystal growth on Si(001) is impossible because of thermodynamical instability of the interface.[8,9,16] Furthermore, in most cases, a lattice mismatch between a substrate and a film prohibits epitaxy. This is why the recently discovered possibility of maintaining $SrTiO_3$ (STO) epitaxial films on the Si(001) and subsequent use of these films as a template for epitaxy of various metal oxides opens new horizons in micro- and nanoelectronics.[7–17]

From a thermodynamical point of view, the interface between the Si(001) substrate and STO film is found to be stable,[9] and thus, due to a good match between the STO lattice constant (3.90 Å) and a Si(001) surface lattice period along the $\langle 110 \rangle$ direction (3.84 Å), a direct epitaxy seems quite probable. However, the direct growth of STO on Si(001) can be accomplished only with a special variable temperature approach.[10–15] A key problem here is the behavior of oxygen at the interface. Oxidation of the silicon surface prohibits epitaxy,[7–9] and therefore stability of the first STO layer is a critical issue. To prevent oxygen diffusion to the interface, it was suggested to start growth of the interface with several layers of Sr ("buffer layer").[8,9] A direct epitaxy (that is, without any buffer layer) also should begin with adsorption of a Sr monolayer, but with following oxidation that results, presumably, in formation of a SrO monolayer. In practice, both methods provide STO epitaxial films on Si(001).[8–15] The (001) surface of STO can be terminated with either a SrO or a TiO_2 plane. To obtain a template for TiO_2 epitaxy, however, it is desirable to have just a TiO_2 terminated STO surface, which can be accomplished by special treatment.[18,19]

It is well known that the Si(001) surface tends to reconstruct with formation of the 1×2 structure[20–26] (and, in some cases, also of the 4×2 structure).[20–23] Thus, a local strain field may appear at the $SrTiO_3/Si(001)$ interface, leading to an increased interface energy and thus affecting the growth mode. Hence, the "match" with the STO film cannot be taken for granted and a challenge is how under these circumstances the epitaxy can be obtained. This issue is addressed in the present study by means of total energy minimization (at zero temperature) within the density functional formalism. In particular, formation of the 2×1 Si(001) surface structure, Sr and SrO adsorbed monolayers, and the equilibrium structure of several epitaxial STO layers on the Si(001) support have been explored in the present study.

The electronic structure of the STO epitaxial films on Si(001) has been investigated by x-ray photoemission spectroscopy (XPS).[10,11] In general, the main features of the valence band spectra can be described in terms of the density of states (DOS) of the components of the system. Thus, a superposition of properly adjusted and renormalized electronic spectra of Si and STO,[10,11,19,20] provides a good fit to the electronic spectra of the net system.[11] In other words, these spectra are viewed as a superposition of yields from bulk Si and STO with an account for the chemical shift ("band offset"[7]) due to the contact potential difference. This feature allows for a comparison between the calculated DOS and experiment and therefore provides further insight into the electronic structure of the interface.

II. METHOD OF CALCULATIONS

Geometry optimizaton was achieved by means of force field calculations using the Vienna *ab initio* simulations package (VASP) code.[27] The total energy and forces required

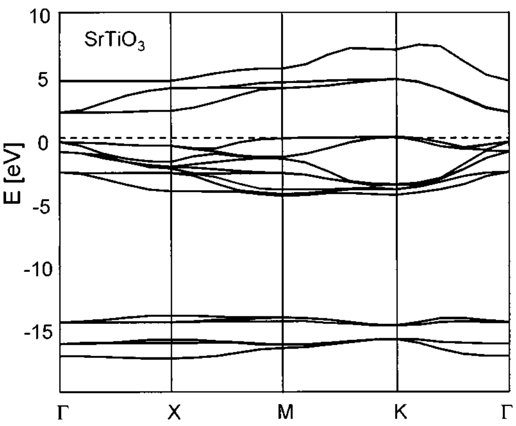

FIG. 1. Band structure of SrTiO$_3$.

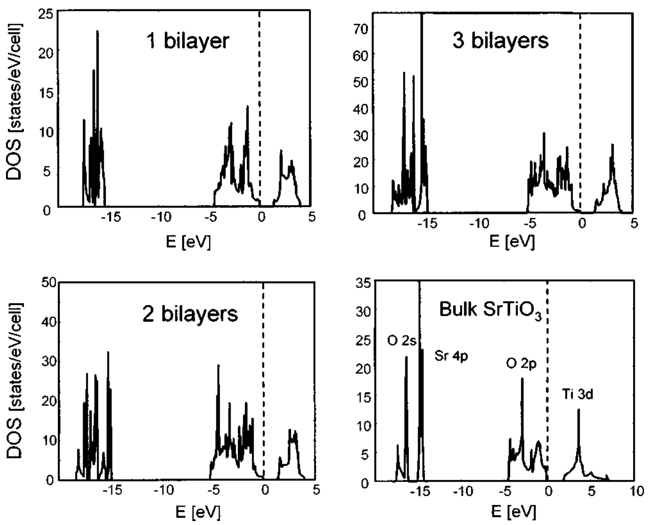

FIG. 2. Densities of states for SrTiO$_3$ “bilayers” (SrO+TiO$_2$) and for bulk SrTiO$_3$.

for the simulations were calculated within the density functional theory (DFT) formalism[28] with exchange-correlation potential in the Perdew-Wang form[29] of the generalized gradient approximation (GGA). To restore periodicity in the direction normal to the surface, a repeat-slab model was adopted, with vacuum gaps of approximately the thickness of the slabs to minimize possible interactions between neighboring slabs. High-precision settings were used throughout to ensure a well-converged calculation. Pseudopotentials were taken in the “ultrasoft” form[30] with energy cutoffs and numbers of plane waves adjusted, for each adsorption system, to provide 1 mRy convergence (typically, for the plane wave basis set, an energy cutoff of approximately 400 eV was used). The 3*p* state of Ti, 4*p* state of Sr, and O 2*s* state were included in the valence set. The DOSs were calculated using the tetrahedral method with the Monkhorst-Pack[31] sets of *k* points ($9\times9\times9$ for bulk phases and $9\times9\times1$ for slabs), with finer meshes in the Brillouin zones for accurate DOS evaluation, after geometry optimizations had been completed.

III. RESULTS

A. Bulk and surface electronic structure of SrTiO$_3$ and 2×1 reconstruction of the Si(001) surface

The lattice constant of bulk STO crystal at equilibrium is found to be 3.94 Å, which is slightly larger than the experimental value 3.90 Å. This difference illustrates a known deficiency of currently available exchange-correlation functionals, with interionic distances being too short within the local density approximation (LDA) and slightly too large within the GGA.[32–38] Another deviation from experiment is underestimation of the width of the band gap (Fig. 1), which appears to be of 2.1 eV [note that recent linearly augmented plane wave (LAPW) calculations[38] have found a gap of 1.6 eV], whereas experimental values vary from 2.9 to 3.3 eV.[10,15] Nevertheless, as discussed below in more detail, the width of the valence band, 4.95 eV (dominated by the O 2*p*-originated band), as well as the binding energies of O 2*s* and Sr 4*p*, are in satisfactory agreement with both experiment[10,19] and other calculations of STO electronic structure.[39]

The STO(001) surface can be either a TiO$_2$ plane or a SrO plane, which terminates the bulk perovskite structure. For more comprehensive analysis of electronic spectra, it is important to reveal changes in the electronic structure of STO that can be attributed to the surface. With this aim in mind, we have performed static self-consistent calculations for STO slabs built from alternate (SrO-TiO$_2$) planes (“bilayers”), which reproduce the perovskite structure with two possible terminations at the (001) surface.

As is seen in Fig. 2, even one bilayer slab retains the main features of the bulk STO electronic structure. In particular, the oxygen 2*s* and 2*p* bands, Sr 4*p*, and Ti 3*d* bands remain almost at the same energy positions as in the case of the bulk STO (the zero energy corresponds to the highest occupied level, which is the Fermi energy E_F at $T=0$). However, the band gap appears substantially decreased as compared with that for the bulk, which can be attributed to a contribution from surface states. This finding is in line with the narrowing of the band gap at STO surfaces reported in Refs. 35–37. With increasing number of bilayers, the DOS gradually approaches that of the bulk STO, while the high-energy shoulder on the plot of the valence band still persists, thus indicating its surface origin.

Hence, the influence of the surface on the DOS of STO is limited to certain changes in the shape of the DOS within the valence and conduction bands. Nevertheless, the qualitative agreement between DOSs calculated for bulk STO and (2–3)-bilayer slabs, suggests that the two-bilayer slab appears to be sufficient to describe the main features of the electronic structure of adsorbed STO films.

Bulk Si. The computed equilibrium lattice constant of bulk Si was found to be 3.87 Å, which coincides with other GGA results,[23–26] while slightly exceeding the experimental value of 3.84 Å.[20–22] As mentioned above, LDA as well as GGA calculations tend to underestimate the band gap.[23–26] This feature is more pronounced for semiconductors—the calculated indirect band gap for Si (Fig. 3) appears to be 0.8 eV, which is in agreement with values obtained in other GGA studies, but considerably smaller than the experimental value

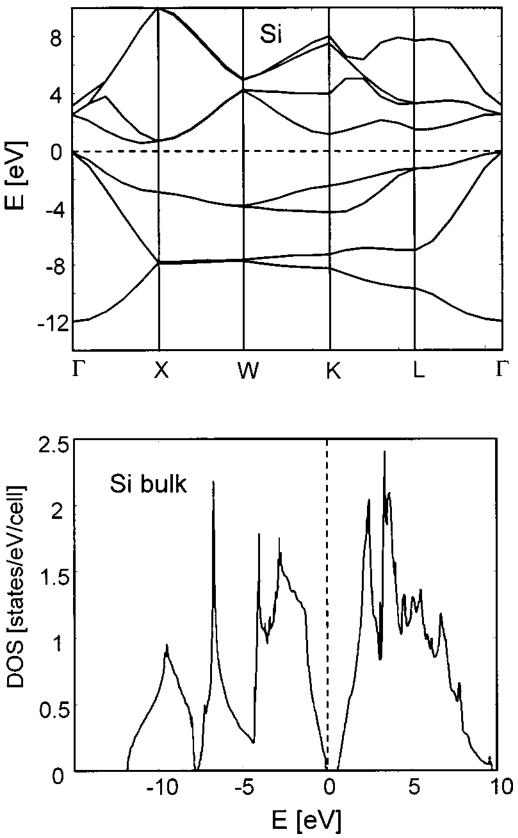

FIG. 3. Band structure and DOS for Si.

of 1.1 eV.[20–22] We will recall this feature in further discussion of the electronic structure of the Si(001) surface and STO adsorbed layers. To this end, it is worth noting that the width of the valence band of Si, approximately 12 eV, is much greater than that of STO (~5 eV; cf. Fig. 2), whereas the DOS peaks for STO have larger amplitudes than those for Si (note the different scales for DOS plots in Figs. 2 and 3). Hence, it may be expected that valence band spectra for STO films on the Si surface will contain a high-intensity region of ~5 eV in width, which originates from STO, and a low-intensity but wide (10–12 eV) band, which originates from the Si substrate.[10]

Reconstruction of the Si(001) surface. Our total-energy static minimization reproduces the well-known 1×2 reconstruction of the Si(001) surface. The driving force of the reconstruction is, obviously, a decrease of total energy. For the 1×2 reconstructed surface, the total energy per Si atom is found to be 0.1 eV lower than for a bulk-terminated (unreconstructed) surface.

In our simulations, we adopted a five-layer slab built from Si(001) planes (Fig. 4). The three upper layers were allowed to relax while the structure of the two lower layers was kept fixed. To account for the possible 1×2 reconstruction, the period of the lattice in the direction across the surface Si rows was doubled, which resulted in ten atoms per unit cell. Another recently suggested reconstruction of the Si(001) surface, $c(4\times2)$,[23] was beyond the purpose of the present study of epitaxial growth of the STO films on Si(001) and thus was not considered.

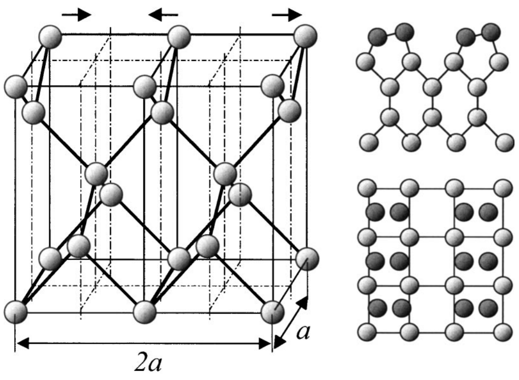

FIG. 4. The unit cell used for simulations of 2×1 reconstruction of the Si(001) surface (left) and "dimerization" of Si atoms at the reconstructed surface (right).

In line with the results of Refs. 20–22, 24, 40, and 41 (but in contrast to calculations in Ref. 42), the reconstructed surface shows buckled dimers of Si atoms (Fig. 4). The reconstruction involves all the three layers, but the changes of positions of the third layer under the reconstruction are found to be very small, which allows for suggestion that the three surface layers are sufficient for modeling of the reconstruction.

In general, both LDA and current GGA functionals tend to underestimate actual values of calculated band gaps in semiconductors,[23,32] and therefore with these methods a small gap between surface states, which might originate from the buckling of surface atomic dimers, might not be amenable to computational characterization. Probably for this reason the reconstructed Si(001) surface remains metallic in the calculations but is semiconducting in experiment.

B. Structures of Sr and SrO monolayers on the Si(001) surface

Sr atoms form linear chains oriented normal to the troughs of the reconstructed Si(001) 2×1 surface. Simulations performed for a monolayer coverage ($\theta=1$) of Sr have revealed a coupling of the Sr chains (Fig. 5), in agreement with the low-energy electron diffraction (LEED) and scanning tunneling microscope[43–46] studies of this system.

The Sr monolayer noticeably suppresses the initial corrugation of the Si(001) surface. However, it does not restore completely the bulk structure of the substrate. Similar behavior has been also reported for Li monolayers on the Si(001) surface.[47] We find that Sr atoms occupy positions about "bridge sites," i.e., are only slightly shifted along the troughs from sites that would be occupied by Si atoms. However, the spacing between the Sr layer and the topmost Si surface layer is substantially increased as compared with the spacing between the Si(001) crystal planes (see Fig. 5). The calculated DOS for the Sr monolayer ($\theta=1$) on the Si(001) surface (Fig. 5) shows a metallic character of this system, as could be expected at high Sr coverages.[48–50]

A critical stage of STO growth on Si(001) is formation of a "template" for epitaxy. It has been found that oxidation of the Si surface can prohibit epitaxial growth of STO. The growth conditions require, however, relatively high

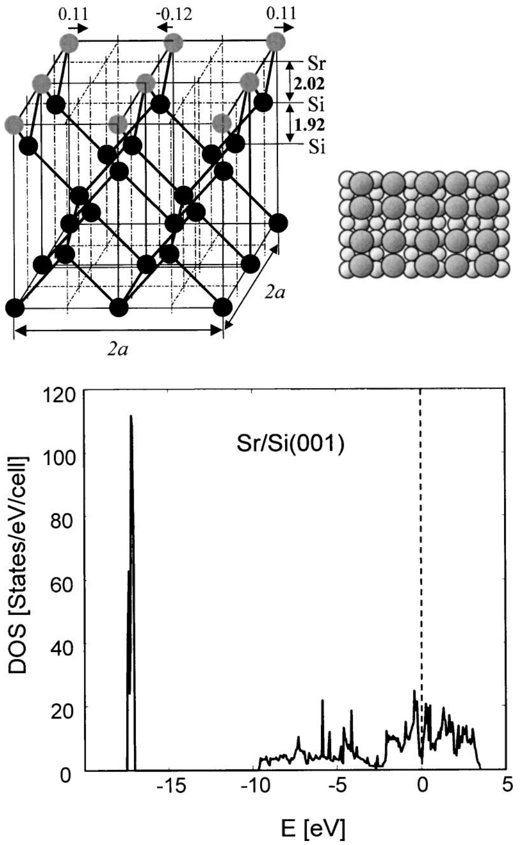

FIG. 5. Structure and DOS for the Sr monolayer on the Si(001) surface.

temperatures[8–17] (200–850 °C). Hence, formation of a stable or metastable film of SrO on Si(001) is critical for the further growth of epitaxial STO films.[8–17]

Our predictions of the atomic and electronic structure of the SrO monolayer on the Si(001) surface are presented in Fig. 6. We underscore two important features of the obtained surface structure: (i) the SrO monolayer completely restores the 1×1 structure of the Si support; (ii) oxygen atoms remain within the SrO layer and therefore do not oxidize the Si(001) substrate surface. Both these features are essential for the successful epitaxy of STO. We conclude that the SrO monolayer on Si(001) is a good template for the epitaxial growth of STO.

It is interesting to note that even in the presence of oxygen, the surface shows clearly metallic character. Figure 6 shows the DOS calculated for a four-layer Si(001) slab covered with SrO from both sides [to exclude a possible "short-cut" by a pure Si(001) surface]. The metallicity of the surface is evident from the noticeable density of states at the Fermi energy. As we will further discuss below, this feature pertains for epitaxial STO films on the Si(001) surface.

C. Electronic structure of SrTiO$_3$ on the Si(001) surface

For these simulations, we built a slab of four planes of Si(001) and two "bilayers" of STO (Fig. 7). Such a choice allows for description of the most important features of the epitaxial STO films on Si(001). In particular, (a) the interface between Si and STO reproduces the SrO layer on Si(001), (b) the topmost surface layer consists of TiO$_2$, as usually observed in experiment,[10,18] and (c) a STO film two "bilayers" thick retains the stoichiometry of the SrTiO$_3$ crystal and has a density of states similar to those of thicker layers (see

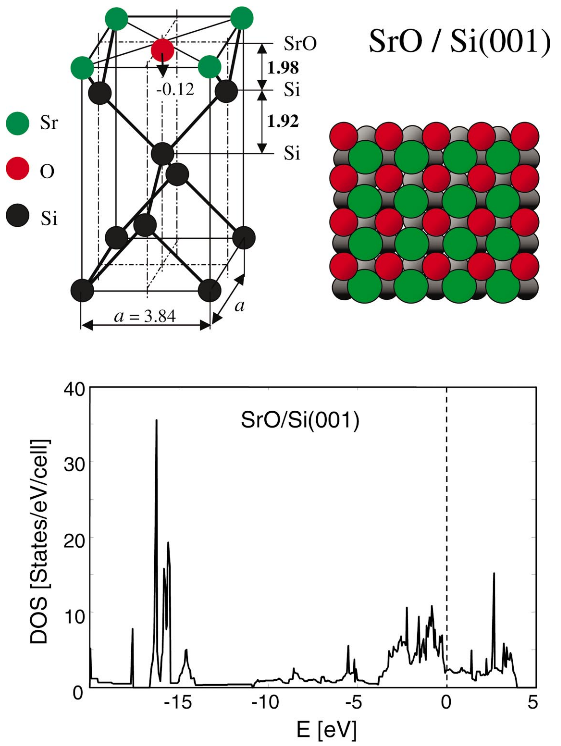

FIG. 6. (Color) Structure and DOS for the SrO monolayer on the Si(001) surface.

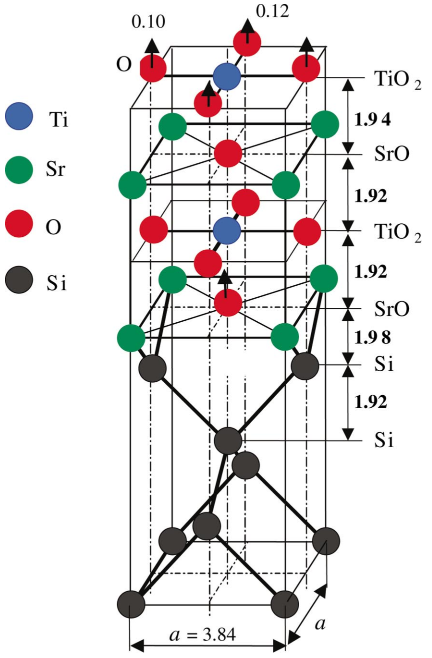

FIG. 7. (Color) The unit cell used for simulations and structure of the SrTiO$_3$ film on the Si(001) surface.

Fig. 2). After relaxation of the system, we increased the thickness of the slab to justify that only minor changes in DOS could be obtained with thicker films.

For simulation of the relaxation of the STO films on Si(001) we used the selective dynamic method, which allows for the modeling of rearrangement of selected atoms in the unit cell while positions of the other atoms are kept constant. In particular, all atoms of STO and two Si(001) planes at the interface were allowed to relax, whereas two Si(001) planes in the bottom of the slab were kept fixed. The latter condition was adopted to reproduce stability of the Si substrate in real experiments.

Results of the simulation are illustrated in Fig. 7. In general, the STO film demonstrates only a limited relaxation (that is, not a reconstruction) of the SrO-TiO_2 layers, and therefore may indeed be considered as an epitaxial film. Along the normal to the surface, the period of the STO film (Sr-Sr distance of 3.96 Å and Ti-Ti distance of 3.95 Å) appears to be only slightly increased with respect to the calculated bulk lattice constant of STO (3.94 Å). The interfacial oxygen atoms from the SrO plane have moved by ~ 0.05 Å toward STO (upward in Fig. 7), which is a favorable feature in the context of the undesirable silicon oxidation. The surface oxygen atoms, which belong to the top TiO_2 layer, tend to shift the STO outward, and different values of their shifts with respect to the Sr plane result in a certain roughening of the surface.

Our results agree in general with earlier calculations of the STO surface relaxation by Heifets *et al.*,[35–37] but, in contrast to the results of modeling performed in Refs. 35–37, 51, and 52, we have found an outward displacement of oxygen atoms in the top TiO_2 layer, in agreement with the LEED, reflection high-energy electron diffraction (RHEED), and medium-energy ion scattering (MEIS) measurements.[53–55] Actual displacement of surface oxygen atoms (“surface rumpling”) at a metal oxide surface depends on subtle details of interionic interactions, as has recently been demonstrated by DFT calculations for MgO and CaO (100) surfaces.[38]

There is an open question whether the STO thin layer on Si(001) is kinetically or thermodynamically stable. The possibility of incorporation of oxygen atoms into the topmost Si-Si bond is currently being considered in our group. Our preliminary results indicate that there is a significant activation barrier for oxidation of the Si surface by the SrO monolayer. This barrier is essential for the epitaxial growth of STO. One should also note that our current procedure of total-energy minimization implies zero temperature, whereas the kinetic stability of a metastable structure is usually temperature dependent. The issue of stability of thin STO films on Si(001) will be addressed in our future study.

The density of states calculated for the relaxed STO film on Si(001) is shown in Fig. 8. It is interesting to note that the DOS for STO/Si(001) generally reproduces the DOS for the STO two-bilayer slabs (cf. Fig. 2), but reveals a metallic character of the net system, which is evident from the nonzero DOS at E_F. To exclude the effect of the Si(001) surfaces (in the “bottom” of the unit cell shown in Fig. 7), which could result in an apparent metallic state of the net STO/Si(001) system, we have also calculated the DOS for a layered superlattice built from five layers of Si(001) and five planes of STO, thus excluding any vacuum region. In this case there is no free Si(001) surface. Thus, the nonzero density of states at E_F, found from these calculations, originates from the STO/Si(001) interface, and, because both the SrO- and TiO_2-terminated STO slabs are definitely dielectric (see Fig. 2), the metallicity of the STO/Si(001) interface originates from the metallic state of the SrO/Si(001) interface.

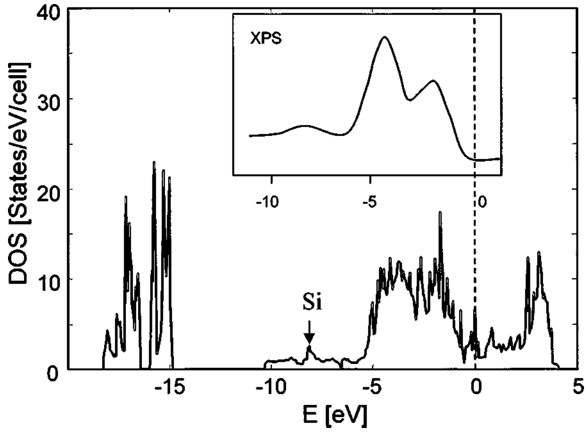

FIG. 8. Densities of states for the $SrTiO_3$ film on the Si(001) surface. The XPS data from Ref. 11 are shown in the inset.

From comparison with the XPS experimental spectrum (shown in the inset in Fig. 8) it is evident that both in theory and in experiment the yield to the net DOS from the Si substrate is the relatively small, but leads to a substantial increase of the width of the valence band. In particular, the peak marked as “Si” in Fig. 8 is typical just for the STO/Si system.[11] For a pure STO crystal surface, there is no such peak in the spectrum while the calculated DOS is zero for this binding energy (see Fig. 2). Hence, the obtained results confirm suggestions from Refs. 10–15 as to the electronic structure of the STO/Si(001) system, which can be described as a superposition of the (bulk) DOSs of STO and Si, with corresponding band offset,[11] whereas some extra features appear, probably due to the interface and surface electronic structures.

IV. SUMMARY

We have performed density functional theory simulations with the Perdew-Wang exchange correlation functional for the $SrTiO_3/Si$ interface. A critical stage of $SrTiO_3$ growth on the Si(001) surface is formation of an interface layer which can serve as a template for subsequent epitaxy and prevents oxidation of the Si substrate surface. Our results for the SrO monolayer on the Si(001) 2×1 surface have revealed a “backward” surface reconstruction which results in the 1×1 structure of the SrO/Si(001) interface, thus providing the almost perfect lattice match essential for epitaxial growth of $SrTiO_3$ films. It has also been found that the interface oxygen atoms remain within the SrO layer and therefore there is a barrier for oxidation of the Si(001) substrate by the SrO layer.

The $SrTiO_3/Si(001)$ interface was found to be metallic and the metallicity has been attributed to the SrO/Si(001) interfacial layer. Because of the low density of states at the Fermi level, we cannot exclude, however, that this result, which means serious consequences for some device applications such as the use of STO as a gate dielectric, may be due to underestimation of the band gap, which is characteristic of the DFT/GGA approach. A metallic interface would be easily detectable in an electrical measurement, but the properties of the interface should depend strongly on the degree of doping of the Si substrate.

In future work we will concentrate on the stability of thin films of STO on Si(001). The incorporation of oxygen atoms into the topmost Si-Si bond should be explored. The height of the activation barrier will be studied as a function of the Sr coverage.

ACKNOWLEDGMENTS

We would like to thank S. A. Chambers, M. A. Henderson, P. A. Dowben, J. E. Jaffe, and M. Dupuis for valuable comments and fruitful discussions. This work was supported by the DOE Office of Basic Energy Sciences, Chemical Sciences Program. Some calculations have been performed at the National Energy Research Scientific Computing Center (NERSC). PNNL is operated by Battelle for the U.S. DOE under Contract No. DE-AC06-76RLO 1830.

---

*Electronic address: maciej.gutowski@pnl.gov

[1] M. Ziese, Rep. Prog. Phys. **65**, 143 (2002).

[2] H. Dulli, E. W. Plummer, P. A. Dowben, J. Choi, and S. H. Liou, Appl. Phys. Lett. **77**, 570 (2000).

[3] C. N. Borca, B. Xu, T. Komesu, H.-K. Jeong, M. T. Liu, S. H. Liou, and P. A. Dowben, Surf. Sci. Lett. **512**, L346 (2002).

[4] T. Obata, T. Manako, Y. Shimakawa, and Y. Kubo, Appl. Phys. Lett. **74**, 290 (1999).

[5] Y. Lu, X. W. Lee, G. O. Gong, G. Xiao, A. Gupta, P. Lecoeur, J. Z. Sun, Y. Y. Wang, and V. P. Dravid, Phys. Rev. B **54**, R8357 (1996).

[6] J. M. De Teresa, A. Barthelemy, A. Fert, J. P. Contour, F. Montaigne, and P. Seneor, Science **286**, 507 (1999).

[7] A. Franciosi and C. G. Van de Walle, Surf. Sci. Rep. **25**, 1 (1996).

[8] R. A. McKee, F. J. Walker, M. B. Nardelli, W. A. Shelton, and G. M. Stocks, Science **300**, 1726 (2003).

[9] R. A. McKee, F. J. Walker, and M. F. Chisholm, Phys. Rev. Lett. **81**, 3014 (1998).

[10] S. A. Chambers, Y. Liang, Z. Yu, R. Droopad, and J. Ramdani, J. Vac. Sci. Technol. A **19**, 934 (2001).

[11] S. A. Chambers, Y. Liang, Z. Yu, R. Droopad, J. Ramdani, and K. Eisenbeiser, Appl. Phys. Lett. **77**, 1662 (2000).

[12] K. Eisenbeiser, J. M. Finder, Z. Yu, J. Ramdani, J. A. Curless, J. A. Hallmark, R. Droopad, W. J. Ooms, L. Salem, S. Bradshaw, and C. D. Overgaard, Appl. Phys. Lett. **76**, 1324 (2000).

[13] G. Y. Yang, J. M. Finder, J. Wang, Z. L. Wang, Z. Yu, J. Ramdani, R. Droopad, K. Eisenbeiser, and R. Ramesh, J. Mater. Res. **17**, 204 (2002).

[14] Y. Wei, X. M. Hu, Y. Liang, D. C. Jordan, B. Craigo, R. Droopad, Z. Yu, A. Demkov, and W. J. Ooms, J. Vac. Sci. Technol. B **20**, 1402 (2002); H. Li, X. Hu, Y. Wei, Z. Yu, X. Zhang, R. Droopad, A. Demkov, J. Edwards, Jr., K. Moore, and W. Ooms, J. Appl. Phys. **93**, 4521 (2003).

[15] J. Robertson and C. W. Chen, Appl. Phys. Lett. **74**, 1168 (1999).

[16] D. G. Schlom and J. H. Haeni, MRS Bull. **27**, 198 (2002).

[17] T. Higuchi, Y. X. Chen, J. Koike, S. Iwashita, M. Ishida, and T. Shimoda, Jpn. J. Appl. Phys., Part 1 **41**, 6867 (2002).

[18] G. Koster, B. L. Kropman, G. J. H. M. Rijinders, and D. H.A. Blank, Appl. Phys. Lett. **73**, 2920 (1998).

[19] T. Nishimura, A. Ikeda, H. Namba, T. Morishita, and Y. Kido, Surf. Sci. **421**, 273 (1999).

[20] D. Haneman, Rep. Prog. Phys. **50**, 1045 (1987); H. Neergaard and J. T. Yates, Chem. Rev. (Washington, D.C.) **95**, 1589 (1995); J. Dabrowski and M. Scheffler, Appl. Surf. Sci. **56**, 15 (1992).

[21] C. J. Wu and E. A. Carter, Phys. Rev. B **45**, 9065 (1992); R. A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992); H. Tochihara, T. Amakusa, and M. Iwatsuki, Phys. Rev. B **50**, 12 262 (1994).

[22] A. K. Rappe, T. A. Smedley, and W. A. Goddard, III, J. Phys. Chem. **85**, 1662 (1981).

[23] G. P. LaFemina, Surf. Sci. Rep. **16**, 133 (1992); J. Dabrowski and H.-J. Mussig, *Silicon Surfaces and Interfaces* (World Scientific, Singapore, 2000).

[24] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985); R. J. Hamers, Ph. Avouris, and F. Bozso, *ibid.* **59**, 2071 (1987).

[25] J. Shoemaker, L. W. Burggraf, and M. S. Gordon, J. Chem. Phys. **112**, 2994 (2000).

[26] P. Kratzer, B. Hammer, and J. K. Norskov, Phys. Rev. B **51**, 13 432 (1993).

[27] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[28] W. Kohn, L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[29] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986); J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. Pederson, D. J. Singh, and C. Fiolhais, *ibid.* **46**, 6671 (1992).

[30] D. H. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).

[31] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[32] J. E. Jaffe, M. Dupuis, and M. Gutowski, Phys. Rev. B **69**, 205106 (2004).

[33] J. C. Woicik, E. J. Nelson, L. Kronik, M. Jain, J. R. Chelikowsky, D. Heskett, L. E. Berman, and G. S. Herman, Phys. Rev. Lett. **89**, 077401 (2002).

[34] I. I. Oleinik, E. Y. Tsymbal, and D. G. Pettifor, Phys. Rev. B **65**, R020401 (2001).

[35] E. Heifets, R. I. Eglitis, E. A. Kotomin, J. Maier, and G. Borstel, Phys. Rev. B **64**, 235417 (2001).

[36] E. Heifets, R. I. Eglitis, E. A. Kotomin, J. Maier, and G. Borstel, Surf. Sci. **513**, 211 (2002).

[37] E. Heifets, E. A. Kotomin, and G. Borstel, Surf. Rev. Lett. **6**,

1215 (1999).

[38] D. R. Alfonso, J. A. Snyder, J. E. Jaffe, A. C. Hess, and M. Gutowski, Phys. Rev. B **62**, 8318 (2000).

[39] O. V. Krasovska, E. E. Krasovskii, and V. N. Antonov, Solid State Commun. **97**, 1019 (1996).

[40] B. Konecny and D. J. Doren, J. Chem. Phys. **106**, 2426 (1997).

[41] A. R. Brown and D. J. Doren, J. Chem. Phys. **109**, 2442 (1998).

[42] A. Redondo and W. A. Goddard III, J. Vac. Sci. Technol. **21**, 344 (1982); B. Paulus, Surf. Sci. **202**, 195 (1998).

[43] A. Herrera-Gomez, F. S. Aquirre-Tostado, Y. Sun, P. Pianetta, Z. Yu, D. Marshall, R. Droopad, and W. E. Spicer, J. Appl. Phys. **90**, 6070 (2001).

[44] R. A. McKee, F. J. Walker, and M. F. Chisholm, Phys. Rev. Lett. **81**, 3014 (1998).

[45] R. Z. Bakhtizin, J. Kishimoto, T. Hashizume, and T. Sakurai, J. Vac. Sci. Technol. B **14**, 1000 (1996).

[46] W. C. Fan, N. J. Wu, and A. Ignatiev, Phys. Rev. B **42**, 1254 (1990).

[47] C. Y. Kim, K. S. Shin, K. D. Lee, and J. W. Chung, Surf. Sci. **324**, 8 (1995).

[48] I. N. Yakovkin, J. Nanosci. Nanotechnol. **1**, 357 (2001).

[49] Y. Morikawa, K. Kobayashi, and K. Terakura, Surf. Sci. **283**, 377 (1993).

[50] T. Abukawa and S. Kono, Phys. Rev. B **37**, 9097 (1988).

[51] J. Padilla and D. Vanderbilt, Phys. Rev. B **56**, 1625 (1997).

[52] J. Padilla and D. Vanderbilt, Surf. Sci. **418**, 64 (1998).

[53] N. Bickel, G. Schmidt, K. Heinz, and K. Muller, Phys. Rev. Lett. **62**, 2009 (1989).

[54] T. Hikita, T. Hanada, M. Kudo, and M. Kawai, Surf. Sci. **287/288**, 377 (1993).

[55] A. Ikeda, T. Nishimura, T. Morishita, and Y. Kido, Surf. Sci. **433–435**, 520 (1999).