Substrate effects on $V_2O_3$ thin films

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Abstract

We apply density functional theory and the augmented spherical wave method to analyze the electronic structure of $V_2O_3$ in the vicinity of an interface to $Al_2O_3$. The interface is modeled by a heterostructure setup of alternating vanadate and aluminate slabs. We focus on the possible modifications of the $V_2O_3$ electronic states in this geometry, induced by the presence of the aluminate layers. In particular, we find that the tendency of the V 3$d$ states to localize is enhanced and may even cause a metal-insulator transition.

Key words: density functional theory, electronic structure, $V_2O_3/Al_2O_3$ heterostructure

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1 Introduction

$V_2O_3$ is a classical example of a material which is located in the vicinity of a Mott transition. The latter can be triggered, for example, by Cr-substitution [1] or by the application of external pressure [2]. In this respect depositing thin films of $V_2O_3$ on a substrate with a slightly smaller in-plane lattice parameter $a$ is likely to provide another way of inducing a Mott insulator-to-metal transition. Indeed, $V_2O_3$ thin films are nowadays attracting great attention, since they promise further insight into the mechanism of the Mott transition [3,4]. In this context, the observation of a thickness-dependent metal-insulator transition (MIT) in ultrathin films has been attributed to an increasing $c/a$ lattice parameter ratio (decreasing $a$, increasing $c$) because of interaction with the Al$_2$O$_3$ substrate [5]. In contrast, detailed X-ray diffraction experiments for high quality films indicate a more complex thickness-dependence of the lattice parameters [6]. In particular, they do not point to systematic changes of the $c$ lattice constant for film thicknesses ranging from 100 Å to 1000 Å.

In this Letter, we aim at clarifying the influence of the substrate on the electronic states of $V_2O_3$ thin films grown on Al$_2$O$_3$. Indeed, for ultrathin films a significant reorganization of the electronic excitations of the film material may be induced by those of the substrate, going beyond geometric effects. In general, the properties of heterointerfaces in many cases deviate considerably from those of the component materials. A prominent example in this context is the quasi two-dimensional electron gas formed at the interface of the insulators LaAlO$_3$ and SrTiO$_3$ [7,8,9]. However, as we will show below, the impact of an Al$_2$O$_3$ interface on the near-$E_F$ density of states in $V_2O_3$ is rather weak.

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as soon as the heterostructure involves several $V_2O_3$ layers.

To describe the electronic effects, we model the interface as a heterostructure consisting of alternating slabs of the component materials. Comparing the $V 3d$ partial densities of states as resulting from the heterostructure calculation to the corresponding bulk data we find only a weak response of the vanadate to the bonding with the aluminate. However, the reduced dispersion of the $V 3d$ states perpendicular to the layers leads to a narrowing especially of the $a_{1g}$ bands, which might suppress the intrinsic metalicity of $V_2O_3$.

2 Structural and calculational details

The unit cell used for modeling the heterostructure is the canonical threefold hexagonal supercell of the trigonal corundum lattice. It comprises six formula units as well as a stacking of six metal layers along the hexagonal $c$ axis. These layers are separated by layers of O atoms, which form octahedra around the metal atoms. In order to set up the heterostructure, we divide the hexagonal supercell into a $V_2O_3$ domain and an $Al_2O_3$ domain, both consisting of three metal layers as well as the corresponding O layers. The $c$ lattice constants and the fractional coordinates of the atoms in the two slabs are those of bulk metallic $V_2O_3$ [10] and $Al_2O_3$ [11], respectively. In contrast, since $V_2O_3$ is grown on an $Al_2O_3$ substrate, we adopt the $a$ lattice constant of the aluminate for the whole supercell. Because the $a$ lattice constant of bulk $V_2O_3$ is about 3.5% larger as compared to that of bulk $Al_2O_3$, a relevant interface stress is induced, which could modify the V valence states. However, no structural relaxation has been found in the experiments [6]. Since a minor relaxation beyond the experimental resolution does not affect our further conclusions, a
structure optimization consequently is dispensable.

Finally, using periodic boundary conditions we obtain a multilayer structure of alternating V$_2$O$_3$ and Al$_2$O$_3$ slabs, as illustrated in Fig. 1. The O atoms, which form a sublattice of space-filling octahedra, are omitted in this representation, since they maintain the positions of the parent compounds. For further details of the structural aspects of V$_2$O$_3$ and related oxides see Ref. [12] as well as the references given therein. We have checked that our results do not depend on the supercell setup, i.e. the thickness of the supercell in $c$ direction and the thickness of the V$_2$O$_3$ slab.

Our investigation is based on density functional theory within the local density approximation. We use a new full-potential version of the augmented spherical

![Fig. 1. Hexagonal unit cell of the V$_2$O$_3$/Al$_2$O$_3$ heterostructure, as used in the calculations. The light gray and red (b/w: dark gray) spheres denote V and Al sites, respectively. The figure shows six buckled (horizontal) planes of V/Al atoms. For clarity, the O atoms have been omitted. They form the well-known O sublattice of corundum V$_2$O$_3$ and Al$_2$O$_3$, see the detailed description in Ref. [10].](image)
wave method [13,14]. The basis set contains Al 3s, 3p, 3d, O 2s, 2p, and V
4s, 4p, 3d orbitals and is complemented by states of additional augmentation
spheres. Brillouin zone integrations were performed using the linear tetrahe-
dron method on a mesh of up to 264 k-points within the irreducible wedge of
the hexagonal zone.

We point out, that the well-known shortcomings of the local density approx-
imation necessitate a careful analysis of the electronic structure in order to
derive reliable conclusions as strong correlation effects are largely ignored in
this approach. As has been pointed out by Brinkman and Rice and elabo-
rated by others [15,16,17,18], such correlation effects may affect the metallic
behavior especially if narrow bands are present near the Fermi energy. Thus,
the following line of reasoning is closely related to previous work on the phase
transitions in vanadium and titanium oxides [19,20,21] and influenced by the
results of recent LDA+DMFT calculations for bulk V\textsubscript{2}O\textsubscript{3} [22,23].

3 Results and discussion

Turning to the results of our calculations, we compare in Fig. 2 the V 3d partial
densities of states (DOS) of metallic bulk V\textsubscript{2}O\textsubscript{3} to those of the heterostructure.
For a more detailed discussion of the band structure and DOS of V\textsubscript{2}O\textsubscript{3} [21] and
related vanadates [12] we refer the reader to the literature. According to Fig. 2,
even for a V\textsubscript{2}O\textsubscript{3} triple-layer the essential features of the V 3d electronic states
largely resemble those of bulk V\textsubscript{2}O\textsubscript{3}. Besides minor differences of the DOS
shape, the energetic positions of the main peaks are very similar. This holds
for both the (partially occupied) \textit{t}\textsubscript{2g} and the (unoccupied) \textit{e}\textsubscript{g} group of states.
Importantly, these findings are rather independent of small variations of the
V positions, which reflects the strong localization of the V 3d states [24]. In addition, the similarity of the bulk and layer partial densities of states builds on the fact that the p-d hybridization resulting from the covalent bonding between V 3d and O 2p orbitals is similar for both geometries.

In passing, we mention that the Al electronic states resemble those of the bulk aluminate. This is due to the fact that Al₂O₃ is an insulator with a large band gap of about 8.7 eV. For the heterostructure the Al states thus are found far

![DOS graph showing partial V 3d DOS per atom for the metallic phase of V₂O₃ (upper panel) and for a V₂O₃/Al₂O₃ heterostructure (lower panel). The lower panel, representing the average of all V atoms, indicates a band narrowing which affects the whole V₂O₃ slab. Besides, the data point to only minor alterations of the electronic states in a V₂O₃ thin film because of the contact to an Al₂O₃ substrate.](image)

Fig. 2. Partial V 3d DOS per atom for the metallic phase of V₂O₃ (upper panel) and for a V₂O₃/Al₂O₃ heterostructure (lower panel). The lower panel, representing the average of all V atoms, indicates a band narrowing which affects the whole V₂O₃ slab. Besides, the data point to only minor alterations of the electronic states in a V₂O₃ thin film because of the contact to an Al₂O₃ substrate.
below and above the Fermi energy, and are hardly influenced by the V states.

The most important difference between the bulk and triple-layer partial densities of states arises from the slightly reduced bandwidths of the latter, again for both the $t_{2g}$ and $e_g$ bands. A similar band narrowing has been observed for the $t_{2g}$ bands of Cr-doped bulk $V_2O_3$, where it traces back to a reduction of the $d$-$d$ overlap coming along with the antidimerization of the V–V pairs parallel to the hexagonal $c$-axis. In that case, LDA+DMFT calculations have clearly demonstrated that the band narrowing, as induced by the structural changes, drives the metal-insulator transition as soon as the strong electronic correlations, which are only rudimentary covered by the LDA, are properly included [22,23]. Transferring that result to the present situation, we may likewise expect insulating behavior from the reduced bandwidth of triple-layer $V_2O_3$.

This finding should be related to the fact that the $a$ lattice constant used here is by 3.5% smaller than that of bulk metallic $V_2O_3$ and, hence, would be rather in favor of metallic behavior. In addition, the $c$ lattice constant and the fractional coordinates of the atoms in the slab are identical to those of bulk metallic $V_2O_3$, which again would preferably lead to metallic behavior. As a consequence, from purely geometric considerations we would expect a broadening of the $t_{2g}$ bands as compared to bulk metallic $V_2O_3$, which would be in favor of metallicity even in the presence of strong electronic correlations.

Yet, the opposite situation occurs. From this we conclude that the band narrowing in the triple-layer is mainly caused by the reduced $d$-$d$ overlap due to the restricted layer-geometry and only to a lesser degree by lattice parameters and atomic parameters. In fact, variation of the $a$ lattice constant (within a reasonable range) has virtually no effect on the magnitude of the band nar-
rowing. As a consequence, taking into account the effect of strong electronic correlations we would expect insulating behavior for rather thin films and a tendency towards metallicity for thicker films. Indeed, this trend has been observed in the experiments [4,5,6,25].

4 Conclusion

In conclusion, electronic structure calculations for a V$_2$O$_3$/Al$_2$O$_3$ heterostructure point to rather localized V 3$d$ $t_{2g}$ states as compared to the situation in bulk metallic V$_2$O$_3$. Although the interface hardly affects the V$_2$O$_3$ electronic states, reduction of the $t_{2g}$ band width due to reduced d–d overlap perpendicular to the layers may cause an insulating ground state of the system if the strong electronic correlations are taken into account. While this mechanism applies mainly to thin films with a thickness of a few V$_2$O$_3$ unit cells, increase of the film thickness will more likely drive an insulator-to-metal transition.

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References

[1] H. Kuwamoto, J. M. Honig, and J. Appel, Phys. Rev. B 22, 2626 (1980).
[2] P. Limelette, A. Georges, D. Jérome, P. Wzietek, P. Metcalf, and J. M. Honig, Science 302, 89 (2003).

[3] C. F. Hague, J.-M. Mariot, V. Ilakovac, R. Delaunay, M. Marsi, M. Sacchi, J.-P. Rueff, and W. Felsch, Phys. Rev. B 77, 045132 (2008).

[4] B. S. Allimi, M. Aindow, and S. P. Alpay, Appl. Phys. Lett. 93, 112109 (2008).

[5] Q. Luo, Q. Guo, and E. G. Wang, Appl. Phys. Lett. 84, 2337 (2004).

[6] C. Grygiel, Ch. Simon, B. Mercet, W. Prellier, R. Frésard, and P. Limelette, Appl. Phys. Lett. 91, 262103 (2007).

[7] A. Ohtomo and H.Y. Hwang, Nature 427, 423 (2004).

[8] N. Nakagawa, H.Y. Hwang and D.A. Muller, Nat. Mater. 5, 204 (2006).

[9] S. Gemming and G. Seifert, Acta Mat. 54, 4299 (2006).

[10] P. D. Dernier, J. Phys. Chem. Solids 31, 2569 (1970).

[11] D. M. Többens, N. Stüßer, K. Knorr, H. M. Mayer, and G. Lampert, Mat. Sci. Forum 378, 288 (2001).

[12] U. Schwingenschlögl and V. Eyert, Ann. Phys. (Leipzig) 13, 475 (2004).

[13] V. Eyert, Int. J. Quantum Chem. 77, 1007 (2000).

[14] V. Eyert, The augmented spherical wave method – a comprehensive treatment, Lect. Notes Phys. 719 (Springer, Heidelberg, 2007).

[15] W. F. Brinkman and T. M. Rice, Phys. Rev. B 2, 4302 (1970).

[16] J. Spalek, A. Datta, and J. M. Honig, Phys. Rev. Lett. 59, 728 (1987).

[17] J. Bünemann, W. Weber, and F. Gebhard, Phys. Rev. B 57, 6896 (1998).

[18] R. Frésard and M. Lamboley, J. Low Temp. Phys. 126, 1091 (2002).
[19] U. Schwingenschl"ogl, V. Eyert, and U. Eckern, Europhys. Lett. 61, 361 (2003); \textit{ibid.} 64, 682 (2003).

[20] V. Eyert, U. Schwingenschl"ogl, and U. Eckern, Chem. Phys. Lett. 390, 151 (2004).

[21] V. Eyert, U. Schwingenschl"ogl, and U. Eckern, Europhys. Lett. 70, 782 (2005).

[22] K. Held, G. Keller, V. Eyert, D. Vollhardt, and V. I. Anisimov, Phys. Rev. Lett. 86, 5345 (2001).

[23] G. Keller, K. Held, V. Eyert, D. Vollhardt, and V. I. Anisimov, Phys. Rev. B 70, 205116 (2004).

[24] A. I. Poteryaev, J. M. Tomczak, S. Biermann, A. Georges, A. I. Lichtenstein, A. N. Rubtsov, T. Saha-Dasgupta, and O. K. Andersen, Phys. Rev. B 76, 085127 (2007).

[25] C. Grygiel, private communication.