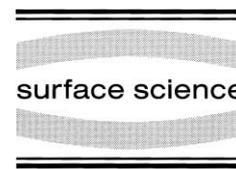




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Surface Science 442 (1999) 251–255



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Structures of pure and Ca-segregated MgO (001) surfaces

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Received 8 April 1999; accepted for publication 5 August 1999

Abstract

The structures of pure and Ca-segregated MgO (001) surfaces have been studied using first-principles density-functional theory. The relaxation and rumpling for the pure surface are found to be 0.48% and 1.62%, respectively. Ca segregation significantly modifies the surface structure. The surface-segregated Ca atoms protrude outwards owing to the size mismatch between Ca and Mg. Consequently, their nearest neighbor oxygen atoms are pulled up. The value of the protrusion of Ca atoms is strongly dependent on the Ca coverage of the surface. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Ab initio calculations; Magnesium oxide; Segregation; Surface

1. Introduction

The MgO (001) surface is widely used as a substrate for the epitaxial growth of superconductors and metals [1–3]. The structure and morphology of the surface play a critical role in the growth of thin films. It is therefore important to understand the details of the surface structure for the growth of high quality thin films. Extensive studies have been carried out on the pure MgO (001) surface both experimentally and theoretically [4–9]. However, a consistent picture for describing the surface structure has not yet been produced. It is known that low concentration of impurities that segregate to the surface can change the structure of the surface, and thus affect the growth of thin films. MgO is a material that is extremely

difficult to purify. It always contains a small amount of impurities (in the parts per million range) such as Al, Ca, C and Fe. Among these impurities, Ca often segregates to grain boundaries and surfaces [10,11]. Very recently, the effects of Ca segregation on the MgO (001) surface have been studied using time-of-flight impact-collision ion scattering spectroscopy (IOF-ICISS), Rutherford backscattering spectroscopy [12], and grazing-incidence X-ray scattering (GIXS) [13]. These studies showed that Ca atoms substitute for Mg atoms at the topmost layer, and protrude outwards owing to the size mismatch between Ca and Mg. However, the value measured by GIXS, 0.63 Å, is much larger than that measured by IOF-ICISS, 0.4 Å. It is reported that the coverage of Ca on the surface of the sample measured by IOF-ICISS is about 20%, while it is about 50% for the sample measured by GIXS. Thus, it is reasonable to speculate that the structure of the Ca-segregated surface is dependent on the coverage of Ca. However, so far, there are neither systematic exper-

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imental studies nor first-principles calculations on the Ca-segregated surface. Only one empirical potential calculation has been carried out by Masri et al. [14]. The purpose of this paper is to investigate the structure of the pure MgO (001) surface, the effect of Ca segregation on the surface and the dependence of the surface structure on the coverage of Ca using first-principles density-functional theory.

2. Method

In our calculations, we use density-functional theory with the exchange-correlation potential treated in the generalized gradient approximation (GGA) [15]. The atomic cores are represented by nonlocal, norm-conserving pseudopotentials in a separable form [16]. The Ca pseudopotential includes the 3p states as valence electrons. We relax the surface structures by a periodic slab geometry. Each slab contains 11 layers and a (001) surface on each side of the slab. The vacuum region between such slabs has a thickness of about 17 Å. To optimize the structure, atoms are relaxed along the calculated forces until the remaining forces are all within $0.1 \text{ eV } \text{Å}^{-1}$. The wave functions were expanded in a plane wave basis set with an energy cutoff of 600 eV and the integration over the Brillouin zone was performed using three special k points chosen according to the Monkhorst–Pack scheme [17]. We calculated the lattice constant for a perfect MgO crystal and the structure of a pure MgO (001) surface using both GGA and local density approximation (LDA) [18]. Consistent results were obtained. The calculated value of the lattice parameter, $a_0 = 4.20 \text{ Å}$, is satisfactorily close to the experimental value of 4.21 Å .

3. Results

We first calculated the structure of the pure MgO (001) surface. The terms rumpling and relaxation are commonly used to describe the structure of metal oxide surfaces. For a pure surface, the perpendicular displacement of anions Z_a and that

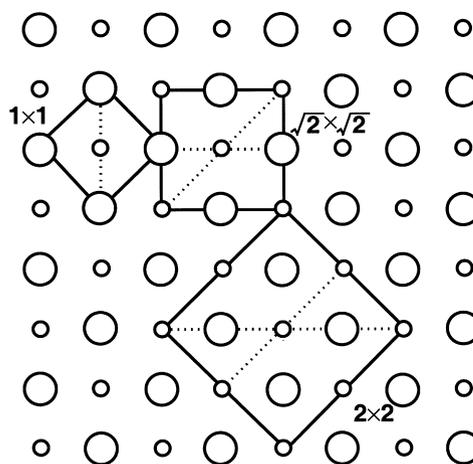


Fig. 1. Structure of the perfect MgO (001) surface showing the 1×1 , $\sqrt{2} \times \sqrt{2}$ and 2×2 cells.

of the cations Z_c can be significantly different. The difference between the displacements $Z_a - Z_c$ is called the surface rumpling, whereas the mean movement of the surface layer ($Z_a + Z_c$)/2 is called the surface relaxation. Normally both are described in percentages of the bulk nearest-neighbor spacing. Our fully relaxed slab shows a very slight rumpling of the surface, with oxygen ions displacing outwards by 0.022 Å and magnesium ions displacing inward by 0.012 Å with respect to the unrelaxed surface. Such displacements occur only at the topmost layer. The values of rumpling and relaxation were calculated to be 1.62 and 0.48%, respectively.

Calculations were then performed on the Ca-segregated MgO (001) surfaces with three coverages of Ca. Ca atoms are considered to substitute for Mg atoms in the top layer. We use three different cell sizes on the surface to represent the coverages of Ca, as shown in Fig. 1. The large circles indicate oxygen atoms and the small ones magnesium atoms. If we substitute Mg with Ca only at the center of these cells, the three cells corresponding to 1×1 , $\sqrt{2} \times \sqrt{2}$ and 2×2 have 100, 50 and 25% coverages of Ca. Because, the calculations are very time consuming, we did not calculate beyond the 25% coverage. Our calculations showed that the segregated Ca not only modifies the topmost layer, but also affects several layers underneath. For each unit cell, sections

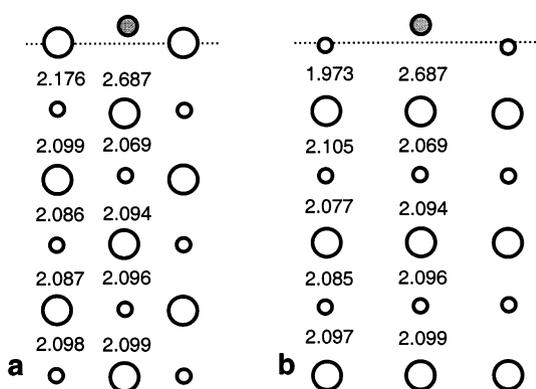


Fig. 2. Atomic positions on (a) (100) section and (b) (110) section of the relaxed $\sqrt{2} \times \sqrt{2}$ structure with 50% coverage of Ca. The dotted lines indicate the position of the unrelaxed surface. The vertical inter-distances are given in Å.

indicated by dotted lines cover all inequivalent sites. Thus, the relaxation below the surface can be described by giving the atomic position in these sections.

Fig. 2 shows the atomic positions on both the (100) and (010) sections for the relaxed $\sqrt{2} \times \sqrt{2}$ structure with 50% coverage of Ca. Ca atoms are indicated by broken circles. It is seen that Ca protrudes outwards by 0.547 Å and its neighboring O on the surface is consequently pulled out by 0.046 Å with respect to the unrelaxed surface, as indicated by dotted lines in Fig. 2. The neighboring Mg on the top layer is pushed inwards by 0.163 Å. The effect of Ca-induced relaxation extends further into the crystal; rearrangements are seen within four layers.

The vertical displacements of atoms of the first two layers of the $\sqrt{2} \times \sqrt{2}$ surface structure with 50% coverage of Ca were measured by Robach et al. using GIXS [13]. Comparison of their mea-

sured and our calculated results is shown in Table 1. It is seen that the calculated values for the protrusion of Ca, 0.547 Å, and the displacement of Mg, -0.163 Å, are slightly smaller than the measured values, 0.63 ± 0.03 and -0.066 ± 0.14 Å, respectively. This difference is probably caused by procedure used to fit the data: the O atoms in the surface and all atoms below the second layer were fixed, which is inconsistent with our calculation. Our relaxed structure (Fig. 2) clearly shows that O atoms in the top layer are pulled outwards by 0.046 Å, and the relaxation extends into the bulk for four layers. If we renormalize the calculated displacements by adding the displacement of O in the top layer, 0.046 Å, the calculated displacements (the forth row in Table 1) for atoms in the top layer agree very well with the experimental data.

Fig. 3 shows the (100) and (110) sections of the relaxed 2×2 surface structure with 25% coverage of Ca. It is seen that the relaxed structure differs from that of the surface with 50% coverage of Ca, as follows. The Ca-induced relaxation extends into the crystal for only three layers. The protrusion of Ca, 0.477 Å, is much smaller than for the $\sqrt{2} \times \sqrt{2}$ structure with 50% coverage of Ca. Oxygen atoms are pulled outwards by 0.073 Å with respect to the unrelaxed surface, slightly smaller than for the $\sqrt{2} \times \sqrt{2}$ structure. The first nearest neighbor Mg in the top layer is pushed inwards by 0.058 Å, while the second nearest neighbor Mg is pushed inwards by 0.009 Å. Souda et al. [12] have measured the structure of the MgO (001) surface with 20% coverage of Ca. The measured value for the Ca protrusion, 0.4 ± 0.01 Å, is only slightly smaller than our calculated value of 0.477 Å, consistent with the slightly reduced coverage of Ca in the experiment.

Table 1

Comparison of measured and calculated vertical displacements of atoms at the first two layers of the $\sqrt{2} \times \sqrt{2}$ structure with 50% coverage of Ca. The numbers labeling the atoms are the same as those used in Ref. [13]

	1:Ca	2:Mg	3:O	4:O	5:Mg	6:Mg	7:O	8:O
exp	0.63 ± 0.03	-0.066 ± 0.14	fixed	fixed	0.20 ± 0.03	-0.42 ± 0.18	-0.42 ± 0.32	0.42 ± 0.12
cal.	0.547	-0.163	0.046	0.046	-0.030	-0.030	-0.036	-0.042
renorm.	0.593	-0.117	0.0	0.0	0.016	0.016	0.010	0.004

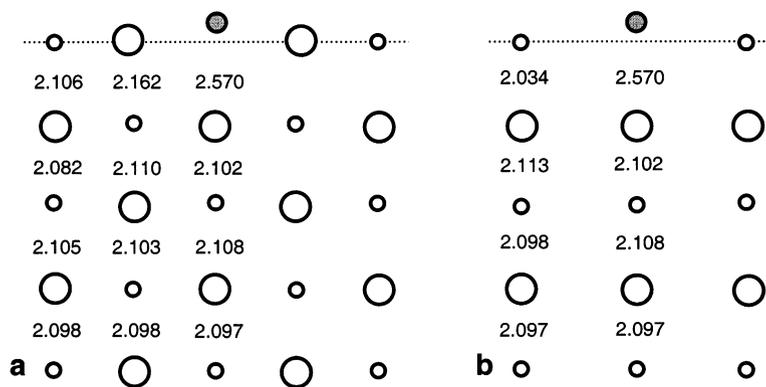


Fig. 3. Atomic positions on (a) (100) section and (b) (110) section of the relaxed 2×2 structure with 25% coverage of Ca. The dotted lines indicate the position of the unrelaxed surface.

To strengthen our conclusion that the Ca-segregated surface structure is dependent on the coverage of Ca, we calculated the surface structure with another coverage of Ca. Fig. 4 shows the atomic positions on the (010) section for the relaxed 1×1 structure with 100% coverage of Ca. As we expected, owing to the higher Ca coverage, the Ca-induced relaxation extends into the crystal for more than five layers. Ca protrudes outwards by only 0.244 Å, but O in the top layer is pulled outwards by 0.071 Å with respect to the unrelaxed surface as indicated by dotted lines in Fig. 4. This again clearly shows that the surface structure is dependent on the coverage of Ca. It should be noted that, below the second layer, both

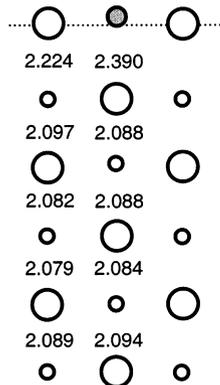


Fig. 4. Atomic positions on (010) section of the relaxed 1×1 structure with 100% coverage of Ca. The dotted lines indicate the position of the unrelaxed surface.

anions and cations are forced to move inwards. This distortion would require a large amount of energy. We therefore expect that the MgO (001) surface with 100% coverage of Ca would never occur experimentally.

4. Conclusions

The density-functional calculations show that the pure MgO (001) surface has a rumpling of 1.62% and a relaxation of 0.48%. Ca segregation significantly roughens the surface. The relaxation induced by Ca segregation propagates further into the bulk crystal. The surface structure is strongly dependent on the coverage of Ca.

Acknowledgements

The work was supported in part by the Division of Materials Science, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation, by an appointment to the Postdoctoral Research Program administered jointly by ORNL and ORISE, and by NSF grant DMR-9803768.

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