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## ADVERTISEMENT



## CrO<sub>2</sub> thin films epitaxially grown on TiO<sub>2</sub> (001): Electronic structure and magnetic properties

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 $CrO_2$  thin films epitaxially grown on the rutile TiO<sub>2</sub> (001) substrate are studied via density function theory. Due to the strain from the substrate, a semiconductor to half-metal transition with the film growth is observed. It is found that, as the film is thicker than three atomic layers, the half-metallic property can be retained with an antiferromagnetic feature which reduces the total magnetic moment. With the help of ionic and the double exchange picture, the physics behind the half-metallic rebuilding process is revealed. © 2011 American Institute of Physics. [doi:10.1063/1.3552991]

#### I. INTRODUCTION

As one kind of typical half-metallic (HM) materials, CrO<sub>2</sub> with nearly 100% spin polarization near the Fermi level  $(E_F)$  has received much attention for spintronics application.<sup>1-6</sup> A limitation is its stability due to the fact that the CrO<sub>2</sub> phase can be easily transformed into more stable  $Cr_2O_3$  phase by the heat treatment.<sup>7</sup> Recently, rutile TiO<sub>2</sub> substrate has been used successfully to stabilize the CrO<sub>2</sub> epitaxial film because of fine lattice match (4% mismatch along the **a**,**b** axis and  $\sim 1.5\%$  along the **c** axis).<sup>8–10</sup> Also, the wide bandgap of about 3.0 eV of TiO<sub>2</sub> makes CrO<sub>2</sub>-TiO<sub>2</sub>-CrO<sub>2</sub> junction good candidate of tunneling magnetosresistance (TMR) device, with an infinite TMR ratio predicted by the Julliére model.<sup>11</sup> Additionally, many studies show that the magnetic properties may change with film thickness,<sup>3,12–15</sup> indicating that the epitaxial film would display different features compared with the bulk phase. To date,  $CrO_2$  film epitaxially grown on the TiO<sub>2</sub> (001) substrate has been successfully prepared by chemical vapor deposition.<sup>7,16</sup> It is well known that the stretching in the  $TiO_2$  (001) surface is larger than that in (100) and (110) ones. Whether the epitaxial film could retain the HM property under the substrateinduced strain has not yet been clarified, and what new feature it would display remains to be explored.

#### **II. CALCULATION DETAILS**

In our calculations, 1–6 layer  $CrO_2$  thin films grown on the TiO<sub>2</sub> (001) substrate are investigated. The slab models are used, in which the vacuum thickness is kept larger than 10 Å. The generalized gradient approximation (GGA) is applied for exchange-correlation effects, and the projector augmented wave potential is used to describe the interaction between atoms and electrons. At the surface Brillouin zone, a 10 × 10 grid of k points is sampled based on the Monkhost–Pack scheme. During the relaxation, we fix three bottom layers of the TiO<sub>2</sub> substrate, and allow all the other atoms to move, until the residual forces acting on atoms are less than 0.01 eV/Å. Since earlier studies show that the correlation effect between the Cr 3*d* electrons would modify the electronic structure of CrO<sub>2</sub> bulk and the (001) surface,<sup>17,18</sup> we also perform DFT+U calculations to improve the reliability of our results.

#### **III. RESULTS AND DISCUSSIONS**

The optimized structures of thin films are shown in Fig. 1. Each film keeps its rutile configuration, expect for a visible relaxation at the surface. In each film, two O atoms at the top layer move along the [110] direction close to the top Cr, and go upward along the [001] axis, while the top Cr atom moves downward. This makes the top Cr stay in a distorted tetrahedron. Moreover, the surface structure changes with the film's thickness. In Table I, the bonds length and angles formed by the O and Cr atoms at the surface are listed. One can see that the bond angle of Cr-O-Cr varies from 129.2° to 113.3° with the film growing. This angle and the O-Cr-O angle decrease rapidly in 1-3 layer films, and is nearly constant in the other thicker films, implying that a stable phase appears. Compared with the unsupported (unstrained) surface structure of CrO<sub>2</sub> obtained by Hong et al.<sup>18</sup> there is a 10° reduction in the O–Cr–O angle for the six-layer epitaxial film, which shows an obvious difference between the strained and unstrained surfaces.

Figure 2 shows the density of states (DOS) of each film. As shown in Fig. 2(a), the one-layer film displays the HM feature. The majority states near the  $E_F$  can be traced to the Cr 3*d* orbitals, while the minority states of Cr 3*d* are directly pushed away from the low-lying O 2*p* states, leaving a gap near the  $E_F$  due to the *d*-*d* exchange interactions. The film's magnetic moment is found to 2.0  $\mu_B$ , consistent with its HM behavior. However, such an HM phase would disappear when the film becomes thicker. As shown in Fig. 2(b), a gap of about 0.4 eV of spin-up states shows that the bilayer film is a narrow-band semiconductor. In Figs. 2(c)–2(f), both spin-up and spin-down states are found to spread across the  $E_F$ , indicating the absence of the HM phase.

The results described above are obtained by the GGA approximation. Next we will take the Hubbard parameter U

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FIG. 1. (Color online) Configurations of thin films with different  $\text{CrO}_2$  layers n (n = 1-6) on  $\text{TiO}_2$  (001) substrate. The light (yellow and silver gray) balls denote Cr and Ti atoms, and the dark (red) balls denote O atoms, respectively. (a)–(f) 1–6 layer  $\text{CrO}_2$  films. (g) The surface configuration of a typical  $\text{CrO}_2$  epitaxial film. Cr1, Cr2, and Cr3 stands for Cr ion in the first, second, and third atomic layers, respectively. (h) The tetrahedral CF around the surface Cr and the Cr 3d splitting type, while (i) shows the octahedral CF around Cr in the deeper layer.

and exchange parameter J into account, to examine the correlation effect on the electronic and magnetic properties of  $CrO_2$  films. The value of U and J are suggested by Korotin et al.<sup>17</sup> to be 3.0 and 0.87 eV, respectively. The electronic structures obtained by these two parameters are in good agreement with the experimental measurements.<sup>5,18</sup> As shown in Figs. 3(a)-3(f), within the DFT+U, a larger splitting gap is found for spin-down states of each film. When the correlation effect is included, the HM phase of the one-layer film is changed to the semiconductor phase. For the bilayer film, the spin-up gap splits further to 1.2 eV. A metal-semiconductor transition happens in the three-layer film. More importantly, in the four-layer and thicker films, the metallic features obtained by the alone GGA calculation becomes the HM phase in the DFT+U calculations. In brief, the semiconductor phase exists in the films within three layers, while the HM phase appears when the film grows thicker, implying a semiconductor-HM transition in the growing process. The total magnetic moment of each film is presented in Table II, which can be described by a simple formula

$$M_{\rm tot} = \begin{cases} 2N\mu_B \ (N=1,2) \\ 2(N-1)\mu_B \ (N\geq 3) \end{cases},$$

where *N* stands for the total layer number of the epitaxial film. This formula is different from that found in the unstrained  $CrO_2$  surface, which shows a direct ratio with *N*.<sup>17,18</sup>

In order to further reveal the HM rebuilding process and find the reason for the reduction of the total magnetic

moment, we discuss below more details of electronic and magnetic properties in the growing process. First, we will show the relationship between electronic structure and geometric structure based on the crystal field (CF) theory. It is well known that in  $CrO_2$  bulk, each  $Cr^{4+}$  is surrounded by six O atoms forming an octahedron. The octahedron splits the Cr 3d orbitals into a  $e_g$  doublet and a low-lying  $t_{2g}$  triplet17-20 based on CF theory.21 However, this picture will change when the  $CrO_2$  (001) surface forms. Due to the removal of two O atoms at the surface, the top Cr becomes four-coordinated. The four neighboring O form a tetrahedron, and the top Cr shifts down and stay in the center of the tetrahedron. According to the CF theory,<sup>21</sup> the tetrahedron makes the  $t_{2\rho}$ - $e_{\rho}$  inversely split [see Fig. 1(h)] which has been found in the unstrained surface.<sup>18</sup> That is to say, the remaining two Cr 3d electrons occupy the low-lying  $e_g$  orbitals, leave the  $t_{2g}$ triplet above  $E_F$  empty, and contribute  $2 \mu_B$ .<sup>18</sup>

In the one-layer epitaxial film, the top Cr provides 2  $\mu_B$ and behaves as Cr<sup>4+</sup>. Such ionic behavior is similar to the result obtained from the unstrained surface.<sup>18</sup> As shown in Fig. 4, the dashed curve shows the local density of states (LDOS) of the Cr 3*d* majority states calculated by the alone GGA method. Very clearly,  $e_g$  and  $t_{2g}$  states are found mainly to be divided by the  $E_F$  with a tiny overlap. When the *U* parameter is included, the  $t_{2g}$  states are fully separated from the  $e_g$  states, leaving a 0.2 eV gap for the CrO<sub>2</sub> surface (see solid curve in Fig. 4). The gap is somehow smaller than the result of 1.2 eV obtained from the unstrained surface.<sup>18</sup> Noticed that the O–Cr–O bond angle (shown in Table I) is

TABLE I. Structural parameters of the supported  $CrO_2$  thin films. Cr-O-Cr and O-Cr-O angles are labeled in Fig.1. "Distance13" is the distance between Cr1 and Cr3 and "distance12" is the distance between Cr1 and Cr2, and so on.

Layers	Cr–O–Cr angle (deg.)	O-Cr-O (deg.)	Distance13 (Å)	Distance12 (Å)	Distance23 (Å)
1	129.2	158.3	2.79	3.37	3.76
2	117.9	142.0	2.69	3.40	3.67
3	113.3	136.7	2.66	3.42	3.61
4	115.1	135.9	2.42	3.38	3.57
5	115.5	136.4	2.42	3.38	3.57
6	114.4	136.0	2.46	3.40	3.56



FIG. 2. (Color online) DOS of the thin films obtained from the alone GGA calculations. (a)–(f) represent 1-6 layer CrO<sub>2</sub> films.

158°, about 8° larger than in the unstained surface, and thus the decrease in the bandgap may be attributed to the distortion of the O tetrahedron. For a Cr ion in an ideal tetrahedron, the O–Cr–O angle is 109.5°, which causes a full splitting between  $t_{2g}$  and  $e_g$  states. When the bond angle increases, the Coulomb interaction between  $e_g$  orbitals and two apex O will become stronger, and therefore reduce the energy difference between  $e_g$  and  $t_{2g}$  states, as well as the bandgap.

We next will discuss the behavior of two-layer  $CrO_2$ film supported on the  $TiO_2$  surface. In Figs. 5(a) and 5(b), we plot the LDOS of the 3*d* states of top Cr and sublayer Cr,



FIG. 3. (Color online) DOS of the thin films obtained from the DFT+U calculations. (a)–(f) correspond to 1–6 layer films.

TABLE II. Electronic properties of 1–6 layer  $\text{CrO}_2$  epitaxial films.  $M_{\text{DFT}+U}$  is the magnetic moment of strained films based on the DFT+U calculations, together with the one of unstrained films  $M_{\text{unstrained}}$  for comparison. As for the conduction type, SC and HM means the semiconductor and half-metallic phase. The corrected band gaps for majority and minority bands are also shown.

Layers	$M_{ m unstrained}$ $(\mu_{ m B})$	$M_{ m DFT+}U}{(\mu_{ m B})}$	Conduction type	Gap <sub>majority</sub> (eV)	Gap <sub>minority</sub> (eV)
1	2	2.00	SC	0.2	1.9
2	4	4.00	SC	1.2	2.1
3	6	4.00	SC	0.3	1.8
4	8	6.00	HM		1.8
5	10	8.00	HM		1.8
6	12	10.00	HM		1.8

respectively. For majority states, a gap of 1.3 eV is found for the top Cr while a 1.2 eV gap for the sublayer Cr. Moreover, the distribution of the occupied states near the  $E_F$  for the sublayer Cr is much more crowded than that for the top Cr, which implies that the sublayer Cr makes a larger contribution to the magnetic moment. The local magnetic moment of the sublayer Cr is 2.9  $\mu_{\rm B}$ , which is much larger than the value of 1.1  $\mu_{\rm B}$  for the top Cr. The above results suggest that the top Cr behaves as a  $Cr^{5+}$  ion, which provides one extra electron to the bond with the neighboring O, while the Cr in the sublayer is in  $d^3$  configuration of  $Cr^{3+}$ . Such charge transfer could also be understood by the change in CF when a surface forms. As shown in Table I, the decrease in the O-Cr-O angle enlarges the O-Cr distance (between top O and sublayer Cr) rapidly to 2.25 Å, which is longer than the distance of 1.69 Å between the O and the top Cr. Thus the O-Cr coordinations are weakened, and the sublayer Cr takes back one more electron around it. Meanwhile, the octahedron CF surrounding the sublayer Cr is also weakened and therefore reduces the energy level of  $t_{2\rho}$ , which is finally occupied by the remaining three electrons below the  $E_F$ . This ionic picture explains the appearance of the 1.2 eV gap in the LDOS of sublayer Cr.



FIG. 4. (Color online) LDOS of the Cr 3d for the one-layer film. The solid (red) and dash (green) curves represent the DFT+U result and the alone GGA one.



FIG. 5. (Color online) LDOS of the Cr 3d for the bilayer film.

For the three-layer and thicker films, the ionic behavior of the Cr at surface can also be found with a similar feature. That is to say, the top two layers cannot provide conduction bands. On the other hand, the well formed O octahedron [see Fig. 1(i)] around the Cr<sup>4+</sup> in the deeper layer (third layer, fourth layer, and so on) splits the 3*d* orbitals with  $t_{2g}$  low-lying, as seen in the CrO<sub>2</sub> bulk.<sup>17–20</sup> However, the reason for the reduced magnetic moment is still unclear. To better understand the magnetic distribution, we show the spin charge density in Fig. 6. First, we found the spin charge density is mainly distributed around the Cr atoms in each film, whereas the TiO<sub>2</sub> substrate displays no magnetism. Second, the magnetic moment provided by each deeper layer Cr is found to be 2  $\mu_{\rm B}$  as in the bulk case, strongly implying that the magnetic reduction is a surface effect. Third, a magnetic moment reversion around the top Cr can be observed when we compare Fig. 6(b) with Fig. 6(c). The reversion is responsible for the total magnetic moment reduction. As identified before,<sup>18</sup> the only 3d electron around the top Cr contributes 1  $\mu_{\rm B}$  to the total magnetic moment. When the spin changes to the opposite direction, 2  $\mu_{\rm B}$  is cut down from the total magnetic moment, and makes an antiferromagnetic (AFM) surface.

This AFM behavior can be interpreted by the Heisenberg model, which has been used to determine the exchange interaction between the  $Cr^{4+}$  ions in bulk  $CrO_2$ .<sup>22</sup> In this model the exchange energy between the neighboring atoms can be described as  $E_{ij} = -A_{ij}\vec{S}_i \cdot \vec{S}_j$ , where  $\vec{S}_i, \vec{S}_j$  correspond to the spin angular momentum of the electron in atoms *i*, *j*, and  $A_{ij}$  corresponds to the exchange integral. The prefactor  $A_{ij}$  is very sensitive to the distance between atoms *i* and *j*.

Table I lists the distance between the top Cr and the nearest Cr (Cr ion in the third layer), which is labeled as "Distance13." When the film grows to three atomic slices, the Distance13 is found to be 2.66 Å, which is smaller than the value of 2.92 Å in the bulk phase. This reduction in the distance makes  $A_{ij}$  negative, and finally leads to an AFM coupling at the surface.

In our calculation, the half-metallic property seems to be rebuilt when the layer number increases to 4. This can be attributed to the appearance of the bulk phase. According to the double exchange mechanism, in bulk, the  $t_{2g}$  orbitals provided by different Cr are strongly coupled with O 2p orbital, which builds the conduction bands.<sup>10,17</sup> We show the band structure of the films in Fig. 7, where (a)-(d) correspond to one-layer, three-layer, four-layer, and six-layer epitaxial film, respectively. In Figs. 7(a) and 7(b), one can see that films thinner than three atomic slices are semiconductor. When the CrO<sub>2</sub> layer number increases to four, two spin-up bands are found to cross the  $E_F$  [see Fig. 7(c)]. These two bands originate from the  $t_{2g}$  orbitals of the Cr in the third and fourth layer (partially from O 2p), implying that the double exchange process begins to take place. Also, these two bands induce the semiconductor-HM transition. As the film thickness grows further, more spin-up bands are found to couple with each other near the  $E_F$  and finally make the HM behavior of the strained film strengthened, as shown in Fig. 7(d).

Furthermore, a highly dispersive band (marked with red dots) can be seen below the  $E_F$  in each film. We find that this band mainly arises from the bottom surface of the TiO<sub>2</sub> substrate, which would reduce the gap width of minority state. This could be considered as a model effect, and the gap width of each slab needs to be corrected. The corrected bandgap is shown in Table II.

#### **IV. CONCLUSION**

First principle calculations are carried out for the  $CrO_2$ thin films epitaxially grown on the  $TiO_2$  (001) substrate. We find the  $TiO_2$  substrate plays an important role in determining the electronic properties of the epitaxial film. On one hand, it helps the  $CrO_2$  layers to keep the rutile structure. On the other hand, the strain from the  $TiO_2$  substrate changes the electronic structure of  $CrO_2$  (001) surface significantly, and leads to an AFM surface for the three-layer and thicker films. The AFM behavior can be considered as a straininduced surface effect, and if the film is thicker than three atomic layers, the Cr ions in the deeper layers would behave as in the bulk phase. With the growing number of the  $CrO_2$ layers, the double exchange process between the Cr 3d electrons begins to take place, and finally rebuilds the half-



FIG. 6. (Color online) Spin charge density of each film. (a)–(f) represent 1–6 layer  $CrO_2$  films.



FIG. 7. (Color online) Band structures of each film. (a)–(d) represent one-layer, three-layer, four-layer, and six-layer films, respectively. Up and down arrows represent the majority and minority spin bands.

metallic property and increases magnetic moment. Our results will be of significant importance in the preparation and spintronics application of CrO<sub>2</sub> thin films.

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