# Bulk and surface physical properties of a $CrO_2$ thin film prepared from a $Cr_8O_{21}$ precursor

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We have prepared a $CrO_2$ thin film by chemical vapor deposition from a $Cr_8O_{21}$ precursor and studied the bulk and surface physical properties. The $CrO_2$ thin film is grown on a $TiO_2$ (100) substrate by heating of a $Cr_8O_{21}$ precursor and $TiO_2$ (100) substrate together in a sealed quartz tube. The prepared film is found from x-ray diffraction analysis to be an (100)-oriented single phase. The magnetization and resistivity measurements indicate that the film is a ferromagnetic metal with a Curie temperature of about 400 K. Cr $3s$ core-level and valence band photoelectron spectroscopy spectra reveal the presence of a metallic $CrO_2$ in the surface region of the film. Our work indicates that preparation from a $Cr_8O_{21}$ precursor is promising for obtaining a $CrO_2$ thin film with the metallic surface. © *2010 American Institute of Physics*. [doi:10.1063/1.3471811]

## I. INTRODUCTION

Chromium dioxide $CrO_2$ is a ferromagnetic metal with a Curie temperature $T_C$ of about 400 K. This is interesting in itself because metallic and ferromagnetic behaviors are rarely found together for $3d$ transition metal oxides: most oxides exhibit strong insulating and antiferromagnetic characteristics. Motivated by the unique characteristics, intensive experimental and theoretical works have been devoted to understanding the physics of $CrO_2$. So far, it is considered that the double exchange interaction between localized Cr $3d$ electrons via intermediate oxygen plays a crucial role for the simultaneous occurrence of metallic behavior and ferromagnetism.[1,2] $CrO_2$ has also attracted considerable attention because it is a half-metallic band structure fully spin-polarized at the Fermi level.[3] Several classes of materials are predicted to have this half-metallic ferromagnetic property, including the Heusler alloys and magnetites $Fe_3O_4$. Of all of the half-metallic ferromagnetic materials, $CrO_2$ is presently the only material with experimentally proven spin polarization close to 100% as measured Andreev reflection.[4,5] These results are motivation to use this material in spintronics devices such as magnetic field sensing and information storage.

$CrO_2$ is a metastable phase at ambient conditions. It has been prepared in a form of thin film by thermal decomposition of gaseous $CrO_3$ (extremely hygroscopic and toxic) using chemical vapor deposition (CVD). Because of its high-quality single crystal, the thin film of $CrO_2$ is widely used for fundamental and application researches. However, there is a serious problem about a surface of the films: insulating layer is often formed at the surface of the film. Only a few exceptions have been reported.[6,7] X-ray photoelectron spectros-copy (XPS) studies of the film surface do not find a metallic Fermi edge while the film shows metallic conductivity.[8] Cheng *et al.*[9] have reported that $Cr_2O_3$, which is an insulator and the most stable phase in chromium oxide binary system, is formed at the surface of $CrO_2$ thin film. Although sputtering and annealing of the surface is performed in order to remove the insulating layer, no emission is observed at the Fermi level in XPS measurements.[8] Such an insulating layer prevents us to perform a reliable photoemission spectroscopy study to elucidate the underlying physics in $CrO_2$ and also to develop the spintronics devices using half-metallic nature for applications. Thus it is highly required to prepare $CrO_2$ thin films without any insulating layer up to the surface of the film.

Recently, Ivanov *et al.*[10] report that epitaxial $CrO_2$ thin films are successfully prepared by CVD from a $Cr_8O_{21}$ precursor. Since $Cr_8O_{21}$ is less hygroscopic and less toxic compared with $CrO_3$, it would be a more appropriate precursor. In addition, they have found from low-energy electron diffraction observations that epitaxial growth of rutile-phase $CrO_2$ occurs to the top monolayer of the film.[11] Their results let us have expectation that the surface of the film is metallic. So far, there is no report on bulk and surface physical properties of the film prepared from a $Cr_8O_{21}$ precursor. In this work, we prepare $CrO_2$ thin film using CVD from a $Cr_8O_{21}$ precursor and study the bulk and surface physical properties of the film by means of magnetization, resistivity and XPS.

## II. EXPERIMENT

Powder of $Cr_8O_{21}$ was prepared by heating of $CrO_3$ at 250 °C for 8 h in flowing oxygen.[10] The obtained $Cr_8O_{21}$ precursor was confirmed from powder x-ray diffraction (XRD) measurements to be a single phase. $CrO_2$ thin film was prepared using a CVD method. Single crystal of rutile-

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type TiO$_2$ (100) was used as a substrate. Rutile-type TiO$_2$ is isostructural with CrO$_2$. Lattice parameter $a$ and $c$ of TiO$_2$ is 4.593 Å and 2.959 Å, respectively, both of which are larger than those of CrO$_2$ ($a$=4.419 Å and $c$=2.915 Å). Lattice mismatch between two materials is 3.9% for the $a$-axis and 1.5% for the $c$-axis. The prepared film was examined by powder XRD using monochromated Cu $K\alpha$ radiation (Rigaku RINT-2000/PC). Magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) and a vibrating sample magnetometer (VSM) (Quantum Design SQUID-VSM). Resistivity measurements were carried out using a standard four-point probe method in a Physical Property Measurement System (Quantum Design PPMS). XPS measurements were performed at SPring-8 BL27SU. Monochromated x-ray of 400 eV and 1300 eV was used for the measurements and the total energy resolution was 200 meV and 400 meV, respectively. Before measurements, the film was annealed in a preparation chamber connected to the spectrometer at 200 °C under the vacuum of $10^{-7}$ Pa for 10 min to obtain a clean surface. All the XPS measurements were performed under an ultrahigh vacuum of $10^{-8}$ Pa. The Fermi level position was determined by measuring the Fermi edge of gold. All spectra were taken at room temperature where CrO$_2$ was in ferromagnetic state.

## III. RESULTS AND DISCUSSION

At first, we prepared CrO$_2$ thin film as described in the previous report.[10] Powder of Cr$_8$O$_{21}$ and TiO$_2$ (100) substrate was heated at 260 °C and 360 °C, respectively, for 4–12 h in a two-zone furnace with oxygen flow from a Cr$_8$O$_{21}$ precursor. However, almost no materials were deposited on the substrate. This is probably because a partial pressure of gases produced by thermal decomposition of Cr$_8$O$_{21}$ is lower in our experimental condition than in the experimental condition of previous work and thus thermally decomposed gas species are not sufficiently supplied onto the TiO$_2$ (100) surface for the growth of CrO$_2$ thin film. Then we considered a different way in which a closed system was utilized for preparation. In a closed CVD system, it is possible to increase the partial pressure of gases decomposed from Cr$_8$O$_{21}$ and, therefore, the gas species can be sufficiently supplied onto the TiO$_2$ (100) surface for the growth of CrO$_2$ thin film. Pellet of Cr$_8$O$_{21}$ and TiO$_2$ (100) substrate were wrapped in Ta foil, and sealed in a quartz tube with an atmosphere of air. The materials were heated at 360 °C for 4 h and cooled down to room temperature.

Figure 1 shows an XRD pattern of the prepared thin film. Two distinguished sets of peaks were observed at $2\theta$ =39.19° and 84.26°, and 40.86° and 88.46°. The former is indexed to peaks from TiO$_2$ (200) and (400), respectively. The latter is identified as (200) and (400) diffraction peaks from tetragonal CrO$_2$. No other peaks were observed by XRD analysis, suggesting that the prepared film is an (100)-oriented single phase. The rocking curve of the CrO$_2$ (200) peak showed a full-width at half-maximum of 0.1°, indicating the high crystalline quality of the film. The film thickness was about 3500 Å which was determined from x-ray reflec-
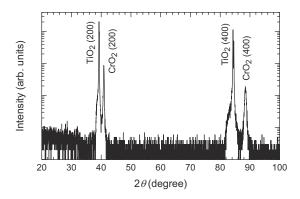


FIG. 1. XRD pattern of a CrO$_2$ thin film on TiO$_2$ (100).

tivity measurements. From XRD analysis, out-of-plane lattice parameter corresponding to the $a$-axis length of CrO$_2$ is found to be 4.415 Å, which is slightly smaller than that of a bulk material (4.419 Å). This compression of the out-of-plane lattice parameter is plausibly due to an in-plane tensile stress induced by a lattice mismatch between the film and the substrate,[12] suggesting that the prepared CrO$_2$ thin film is epitaxially grown on the TiO$_2$ (100) substrate.

Figure 2(a) shows the magnetic field dependence of magnetization for the prepared thin film, measured at 5 and 300 K. Magnetic field was applied along the $b$-axis and $c$-axis directions in the CrO$_2$ (100) surface. At 5 K, the hysteresis with a coercive field of 8 mT was observed, indicative of the ferromagnetic nature of the film. The magnetic easy axis is clearly along $c$-axis while $b$-axis is the magnetic hard axis direction, which is in good agreement with the result reported previously.[12] The saturation magnetization at magnetic field of 1 T was 640 emu/cm$^3$, corresponding close to the full theoretical magnetic moment of 2 $\mu_B$ per Cr ion observed in the bulk. The magnetic hysteresis was still observed in the magnetic hysteresis loops at 300 K, which indicates that the film is ferromagnetic at room temperature. At 300 K, the coercive field was decreased to about 3 mT and the saturation magnetization was reduced to 1.4 $\mu_B$ per Cr ion. The spontaneous magnetization as a function of temperature measured along the $b$-axis direction in an applied magnetic field of 0.5 T is shown in Fig. 2(b). An abrupt increase in the magnetization which corresponds to the Curie temperature $T_C$ was observed at about 400 K. The magnetization decreased as the temperature increased. These results are in good agreement with those reported in CrO$_2$ films.[12,13] The temperature dependence of the resistivity along the $b$-axis direction is shown in Fig. 2(c). For the measurements, we cut the film into thin pieces and evaporated silver electrodes so as to limit the current direction to the respective film-plane axis, namely, $b$-axis. As seen in the figure, the film showed metallic conductivity. The resistivity along the $b$-axis direction is 190 $\mu\Omega$ cm at room temperature and decreased to 29 $\mu\Omega$ cm at 2 K. The residual resistivity is rather high and a room temperature resistance to residual resistance ratio of 6.5 is smaller than that reported in CrO$_2$ thin films on TiO$_2$ (100) substrates.[13] This is probably because of grain boundary scattering.[13] These magnetic and transport measurements reveal that the prepared CrO$_2$ thin film is a ferromagnetic metal with $T_C$ of about 400 K.

FIG. 3. XPS spectrum of Cr $3s$ core-level for a $CrO_2$ thin film on $TiO_2$ (100). The spectrum was taken at the photon energy of 1300 eV.
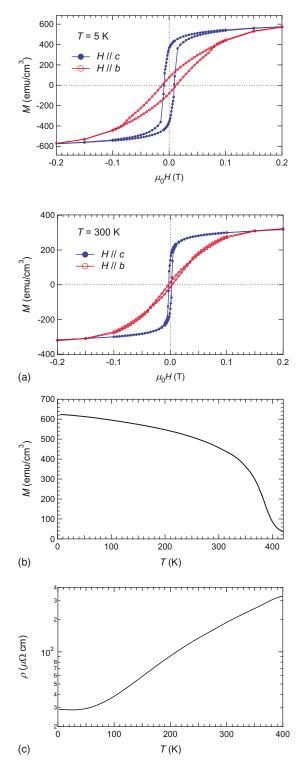


FIG. 2. (Color online) (a) Magnetic hysteresis loop at 5 and 300 K along the $b$-axis and $c$-axis directions, (b) temperature dependence of the magnetization along the $b$-axis direction in an applied magnetic field of 0.5 T, and (c) temperature dependence of the resistivity along the $b$-axis direction for a $CrO_2$ thin film on $TiO_2$ (100).

In order to examine the electronic state of the prepared thin film, XPS measurements were performed. In the measurements, photon energies of 400 and 1300 eV were used. Since the mean free path of photoelectrons for these photon energies is about 1 nm, our XPS measurements provides the electronic state of the film within the depth of the nanometer order from the fil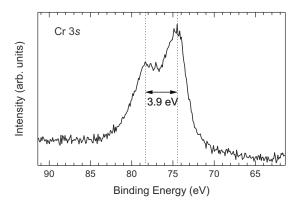m surface. Figure 3 shows the Cr $3s$ core-level spectrum of the film, measured with the excitation photon energy of 1300 eV. Two peak-structures were observable at 74.48 and 78.38 eV. These are the Cr $3s$ exchange splitting originated from the exchange coupling between the Cr $3s$ hole and the Cr $3d$ electrons.[14,15] The peak at 74.48 eV is due to the Cr $3s$ main one and the peak at 78.38 eV is due to the exchange satellite. The peak positions in the obtained Cr $3s$ spectrum is close to those for $CrO_2$ bulk (74.81 and 78.78 eV) rather than $Cr_2O_3$ bulk (75.11 and 79.19 eV).[16] Notice that the exchange satellite interfered with the main line. This spectral feature resembles that for $CrO_2$ bulk compared with that for $Cr_2O_3$ where the satellite is well separated from the corresponding main line.[16] These results indicate that the observed XPS spectrum originates from $CrO_2$. We also measured the Cr $2p$ core-level spectrum of the film (not shown here) and found that the peak positions of Cr $2p_{3/2}$ and Cr $2p_{1/2}$ spectra are in good agreement with those for $CrO_2$ bulk. The results of core-level spectra evidence the presence of $CrO_2$ in the surface region of the film. Figure 4(a) shows the valence band spectrum of the film. In the measurements, the photon energy of 400 eV was used. Since the mean free path of photoelectrons for the photon energy of 400 eV is slightly smaller than that for the photon energy of 1300 eV, it provides more surface sensitive electronic state of the film. As seen in the figure, the valence band spectrum showed a two-peak structure. A peak located at 0–3 eV is mainly due to the Cr $3d$ band and a broad band situated at 3–9 eV is mainly due to the O $2p$ band. The most important fact is that a finite intensity is clearly observed at the Fermi level. This indicates that the surface of the film is metallic. In order to confirm the metallic nature of the film surface, the obtained spectrum was compared with that of gold in the region of the Fermi energy. As seen in Fig. 4(b), the spectrum of the film traces that of gold very well, strongly evidencing that the surface of the film is metallic. So far, there are only a few XPS results that show the metallic nature of the $CrO_2$ thin films.[6,7] For instance, Chang *et al.*[7] showed the valence band spectrum with a finite intensity in the region of the Fermi level in the synchrotron XPS measurements with a photon energy of 385 eV, close to the energy we used. The present results are in good agreement with their results. On the other hand, Ventrice Jr. *et al.*[8] reported recently that no emission at the Fermi level was observed in
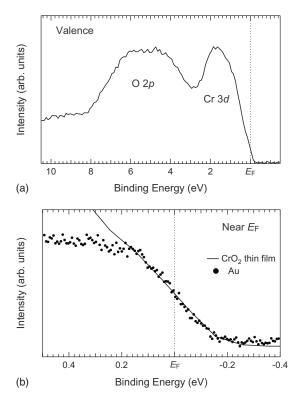
FIG. 4. (a) Valence-band spectrum for a $CrO_2$ thin film on $TiO_2$ (100). (b) Near $E_F$ valence band spectrum of a $CrO_2$ thin film (solid line), together with that of gold (dot) for comparison. Both spectra were normalized by the intensity at $E_F$. The spectra were taken at the photon energy of 400 eV.

more surface sensitive XPS measurement with a photon energy of 75 eV even for the stoichiometric $CrO_2$ surface, and stated that first three or four atomic layers of $CrO_2$ thin film had not metallic nature but semiconducting or semimetalic nature. In order to compare with the results reported by Ventrice Jr. *et al.* and reveal the physical nature of near topmost layer of $CrO_2$ thin film, further XPS study performed with more surface sensitive photon energy is necessary.

Preparation from a $Cr_8O_{21}$ precursor is promising for obtaining a $CrO_2$ thin film with the metallic surface. Also, the result of our preparation in a closed system suggests that the partial pressure of gases which are produced by thermal decomposition of $Cr_8O_{21}$ is an important experimental parameter for obtaining such a film. Further study is under going to obtain information on the growth mechanism of the film. Successful preparation of $CrO_2$ thin film having a metallic surface helps not only perform a reliable photoemission study to understand the physics of $CrO_2$ but also develop the $CrO_2$-based devices using a half-metallic nature for spintronics applications.

## IV. CONCLUSIONS

In summary, we have prepared a $CrO_2$ thin film from a $Cr_8O_{21}$ precursor using CVD and studied the magnetic and electric properties and the electronic state by means of magnetization, resistivity, and XPS. The $CrO_2$ thin film is prepared by heating of a $Cr_8O_{21}$ precursor and $TiO_2$ (100) substrate in a sealed quartz tube. XRD analysis shows that the film is an (100)-oriented single phase. From the magnetization and resistivity measurements, the film is found to be a ferromagnetic metal with a Curie temperature of about 400 K. Analysis of the Cr 3s core-level photoelectron spectroscopy spectrum indicates the presence of $CrO_2$ in the surface region of the film. In addition, the valence band spectrum measurement reveals that the surface of the film is metallic. The present work indicates that the preparation from a $Cr_8O_{21}$ precursor is promising for obtaining a $CrO_2$ thin film with the metallic surface.

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