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Publication Date
2009-08-21

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Epitaxial growth and Characterization of $CaVO_3$ Thin Films

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ABSTRACT

Epitaxial thin films of $CaVO_3$ were synthesized on $SrTiO_3$, $LaAlO_3$ and $(La_{0.27}Sr_{0.73})(Al_{0.65}Ta_{0.35})O_3$ substrates by pulsed laser deposition. All $CaVO_3$ films, independent of epitaxial strain, exhibit metallic and Pauli paramagnetic behavior as $CaVO_3$ single crystals. X-ray absorption measurements confirmed the 4+ valence state for Vanadium ions. With prolonged air exposure, an increasing amount of V^{3+} is detected and is attributed to oxygen loss in the near surface region of the films.

Perovskite vanadium oxides, AVO_3, where A= Ca, Sr, La, or Y exhibit a wide range of intriguing magnetic and electrical properties: from antiferromagnetic to Pauli paramagnetic and from insulating to metallic behavior.[1] By choosing different A cations, it is possible to tune either the *d* bandwidth (e.g. A= Ca, Sr)[2] or the *d*-band filling (e.g. A= La, Ca)[3] affecting the electron-electron correlation and in turn the magnetic and electronic properties. There have been thorough studies of bulk vanadates among the AVO_3 series, and in particular bulk $CaVO_3$ (CVO) has been found to be a Pauli paramagnetic metal with a $3d^1$ electronic configuration. However, small deviations in oxygen content due to variations in growth conditions or air exposure can give rise to Curie-Weiss paramagnetism, antiferromagnetism and/or insulating behavior. Thus, varying oxygen stoichiometry is an alternative way to tune *d* band filling and bandwidth. Epitaxial strain may be another way to vary bandwidth. To date, CVO has been studied only in bulk form but the successful growth of CVO thin films will provide a model system to probe the robustness of the Pauli paramagnetic metallic state.

In this paper we present the growth of epitaxial CVO thin films on $SrTiO_3$ (STO), $(La_{0.27}Sr_{0.73})(Al_{0.65}Ta_{0.35})O_3$ (LSAT) and $LaAlO_3$ (LAO) substrates inducing tensile epitaxial strain in the CVO films between 3.5% and 0.7%. The CVO films exhibit excellent crystallinity and smooth surface morphology. X-ray diffraction (XRD), superconducting quantum interference device (SQUID) magnetometry and electronic transport measurements confirm the synthesis of metallic, Pauli paramagnetic CVO thin films independent of the substrate. X-ray absorption (XA) measurements at the V $L_{2,3}$ edges indicate a 4+ valence state for the V ions. After prolonged exposure to air,

however, the V valence changes to 3+ in the near surface region of the films due to a loss of oxygen at the surface.

CVO thin films were grown on STO, LSAT and LAO (001) substrates by Pulsed Laser Deposition (PLD) using a stoichiometric target. The substrates were held at temperatures between 550°C and 650°C during deposition in vacuum (4.9 $\times 10^{-6}$ Torr). The KrF excimer laser was operated at an energy density of 1.3-1.5 J/cm^2 at 3 Hz. Film thickness ranged from 40 nm to 60 nm. The bulk lattice parameters of CVO, STO, LSAT and LAO are 3.77 Å, 3.905 Å, 3.866 Å and 3.798 Å, respectively. Consequently, the CVO film is expected to grow under tensile epitaxial strain with lattice mismatch of 3.5%, 2.5% and 0.7% for STO, LSAT and LAO, respectively. The surface morphology of the films was characterized by Atomic Force Microscopy (AFM). The crystal structure of the films was evaluated by XRD in the standard θ-2θ geometry. Rutherford Backscattering Spectrometry (RBS) measurements were performed to determine film thickness and estimate the film stoichiometry. However, the CVO sensitivity to oxygen[4-6] and the small backscattering yield of oxygen ions make it very difficult to quantify the oxygen content of CVO samples through RBS experiments precisely. The magnetic and electrical properties have been determined respectively by SQUID magnetometry and transport measurements from 3-300K. X ray absorption (XA) spectra were measured in total electron yield at beamline 6.3.1 of the Advanced Light Source.

In-situ Reflection High Energy Electron Diffraction monitoring the film growth on STO substrates indicated a layer-by-layer growth mode while films deposited on LSAT and LAO were more likely to exhibit 3D island growth. The different growth modes resulted in the smoother surface morphology for STO substrates (typical RMS

roughness of 0.461 nm) than for LSAT (1 nm) and LAO (0.766 nm) substrates. XRD results shown in Figure 1 indicate a CVO single phase and single orientation structure for all thin films independent of substrate. The CVO out-of-plane lattice parameter as derived from the XRD data is approximately 3.75 Å for STO and LSAT and 3.77 Å for LAO. Since all substrates induce a tensile strain in the CVO in its surface plane, the out-of-plane lattice parameter is expected to be smaller compared to the bulk value of 3.77 Å (indicated by a vertical line in Fig. 1). The diffraction peaks for CVO films on STO and LSAT substrates are almost overlapping, despite the difference in magnitude of the tensile strain. Reciprocal-space maps (not presented here) show similar in-plane lattice parameters for equal thickness CVO films on STO and LSAT substrates, thus suggesting different relaxation. RBS data (not shown here) indicate a 1-to-1 ratio for V and Ca in the samples.

Magnetic susceptibilities have been measured as a function of temperature for all zero field cooled (ZFC) CVO films in a 1 kOe magnetic field. Susceptibility measurements are shown with the contributions from the STO, LSAT and LAO substrates subtracted. In order to assess the Pauli paramagnetism we have used the figure of merit χT as a function of the temperature. For Pauli paramagnetism, χT should show a linear behavior in contrast to a constant value expected for a Curie-Weiss paramagnet. The observed linear temperature dependence of χT for all CVO films (Fig. 2(a)) is indicative of a Pauli paramagnet as measured for CVO bulk material.[2-10]

Transport measurements shown in Fig. 2(b) reveal metallic behavior for all CVO films. The temperature dependence of the resistivity can be well described by a

$\rho=\rho_0+AT^2$ dependence as expected for a system dominated by strong electron-electron correlations. The residual resistivity ρ_0 values range from 30-50 μΩcm in agreement with values for CVO single crystal and polycrystalline samples.[2-5,7-12] The residual resistivity may be attributed to a temperature independent grain boundary contribution that shows small variations depending on the substrate. The coefficient of the temperature dependent term, A, ranges from 0.64-0.9 nΩcm/K^2 consistent with previous values found for highly correlated CVO bulk materials. [2,4,5,7]

The magnetic and electronic properties of bulk CVO are very sensitive to the oxygen stoichiometry.[6,7,9,10] Therefore, we can use the observation of Pauli paramagnetism and metallicity to estimate indirectly the oxygen stoichiometry of the samples. In the bulk, $CaVO_{3+\delta}$ exhibits insulating behavior for $\delta>0$ while $\delta<0$ may give rise to a small antiferromagnetic component present in the temperature dependent susceptibility and to localized magnetic moments.[2,3,5,6,9] Given their metallic and Pauli paramagnetic behavior, the CVO thin films can be evaluated qualitatively as being stoichiometric.

The electronic structure of the CVO films was probed by XA at the vanadium $L_{2,3}$ edges and oxygen K edges as shown in Fig. 3(a). In bulk CVO, vanadium has a $3d^1$ electronic configuration. The V d orbitals are hybridized with the oxygen $2p$ states. Both the vanadium $L_{2,3}$ edges and oxygen K edge spectra lineshapes are insensitive to the strain induced by the substrate. A survey of binary vanadium oxides discussed in Ref. 13 (and ref. therein) indicates that the oxygen K edge is particularly sensitive to the valence state of the vanadium cations, while the vanadium $L_{2,3}$ edges are less affected. For V^{5+} ions, we

expect at the O K edge a single peak at about 530 eV plus a shoulder at 532.5 eV. As the V valence state decreases, the first feature decreases while the second increases in intensity with both features shifting to higher photon energy. A comparison of our XA lineshapes in Fig.4 with the data in Ref. 13, suggests that V is present in a V^{4+} valence state independent of the substrate. This result is consistent with the magnetic and electronic properties that point to stoichiometric CVO thin films.

Given the surface sensitivity of the XA measurements in total electron yield mode and the known sensitivity of CVO to exposure to air, we have also evaluated how the electronic configuration changes at the surface due to air exposure in our samples. CVO thin films were measured by XA immediately after the deposition and a second time after a few months of exposure to air. The measurements have been performed both in grazing and normal x-ray incidence and the results are shown in Fig. 3(b). When comparing the normal versus grazing incidence data, it is clear how even immediately after deposition a small difference exists between the surface (grazing incidence) and more bulk (normal incidence) electronic configurations. Using again Ref. 13 as a fingerprint for the V valence state, we find that the surface is a mixture of V^{4+} and V^{3+} while deeper below the surface our samples are closer to a V^{4+} valence state, thus showing the effect of the exposure to air even for a short time. In data collected after few months of exposure to air (Fig. 3(c)), the change in the lineshape is even more pronounced. The normal incidence XA data, i.e. more bulk-like, is now also a mixture V^{4+}/V^{3+} compared to the as-deposited measurement. These spectra also show the expected shift to higher photon energy as the V valence decreases.

In summary, we have successfully synthesized epitaxial thin films of $CaVO_3$ on STO, LSAT and LAO substrates. These films exhibit metallic and Pauli paramagnetic behavior as CVO single crystals. XA data show a clear $3d^1$ electronic configuration for our samples with a 4+ valence state for V ions.

We would like to acknowledge F. Wong for helpful discussions. This work and the Advanced Light Source are supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. RVC acknowledges support from the National Science Foundation.

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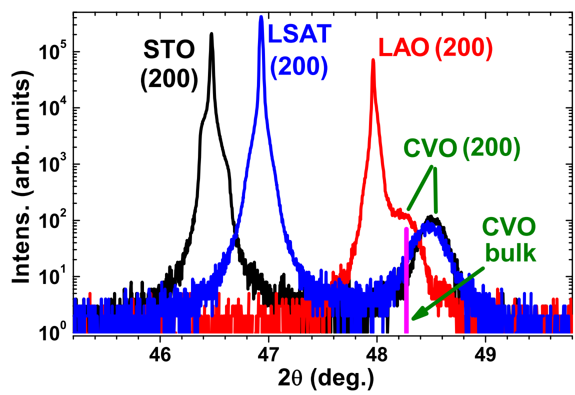
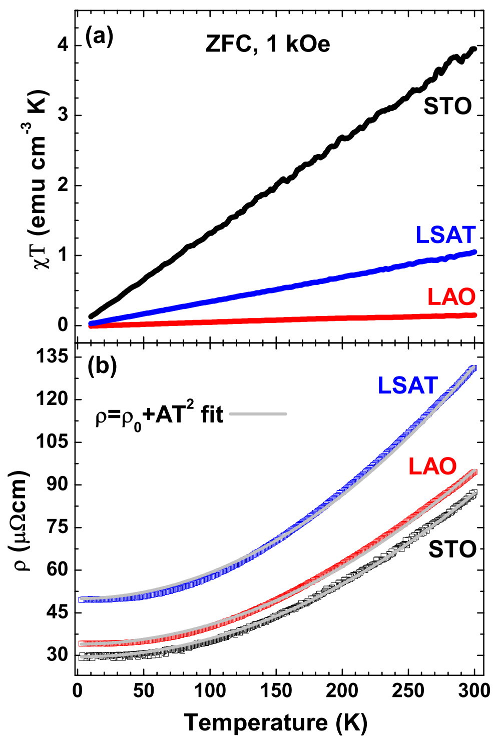
Figure Captions

Figure 1 (Color online): XRD data for 45nm CVO films on STO, LSAT and LAO substrates. The bulk CVO value is also marked.

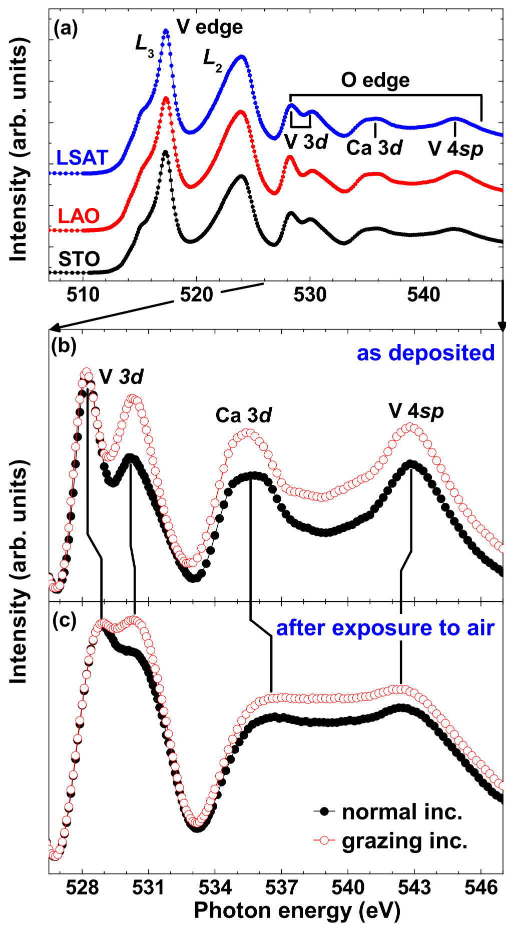
Figure 2 (Color online): (a) Product of the magnetic susceptibility data (ZFC, 1kOe), with substrate contribution subtracted, for the temperature as a function of T for 45nm CVO films on STO, LSAT and LAO substrates. (b) Resistivity as a function of temperature for 45nm CVO films on STO, LSAT and LAO substrates. A $\rho=\rho_0+AT^2$ fit is also shown for all three samples.

Figure 3 (Color online): (a) XA spectra measured at the V $L_{2,3}$ and O K edges for 45nm CVO films on STO, LSAT and LAO substrates. (b) XA spectra obtained in grazing incidence (red squares) and normal incidence (black squares) for a 45nm CVO film on LAO substrate right after the deposition and (c) after prolonged exposure to air.


STO
(200)
LSAT
(200)
LAO (200)
CVO (200)
CVO
bulk
Intens. (arb. units)
2θ (deg.)



(a)
ZFC, 1 kOe
STO
LSAT
LAO
χT (emu cm^-3 K)
(b)
LSAT
ρ=ρ0+AT^2 fit
LAO
STO
ρ (μΩcm)
Temperature (K)


(a)
V edge
L_3
L_2
O edge
LSAT
LAO
STO
V 3d
Ca 3d
V 4sp
Intensity (arb. units)
510
520
530
540
(b)
as deposited
V 3d
Ca 3d
V 4sp
(c)
after exposure to air
normal inc.
grazing inc.
Intensity (arb. units)
528
531
534
537
540
543
546
Photon energy (eV)