DOI: 10.1017/S1431927606068255
Microsc Microanal 12(Supp 2), 2006

Studying Vanadium-based Perovskites by Scanning Transmission Electron Microscopy

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Due to the existence of interesting correlations between structure and properties, vanadium-based perovskites (RVO_3) are attracting considerable attention as a model system for fundamental studies of the interactions between charge, orbital, lattice, and spin degrees of freedom. Due to the different ionic sizes and electronic structures of R, RVO_3 perovskites show widely varying structural distortions and properties. YVO_3, which has an orthorhombic distortion at room temperature, undergoes a first-order structural phase transition at T_S = 77 K [1]. $SrVO_3$, which exhibits a cubic structure, is a metallic oxide which exhibits transport consistent with electron correlations [2]. $PbVO_3$, is a new member of the series recently fabricated under high pressure and high temperature that exhibits a large tetragonal structural distortion and has potential as a multiferroic material [3-4]. However, while the properties of these materials are becoming well known, the understanding of the correlation between microstructure and properties of thin film perovskite vanadates is in its infancy.

Scanning transmission electron microscopy (STEM) was used to investigate the atomic and electronic structures of different thin films vanadium perovskites, including YVO_3, $SrVO_3$ and $PbVO_3$. These thin films were formed on $SrTiO_3$ or $LaAlO_3$ substrates by Pulsed Laser Deposition (PLD). STEM has proven to be a powerful characterization tool for studying microstructures with atomic resolution, in particular by combining Z-contrast imaging and electron energy loss spectroscopy (EELS) [5]. The present experiments were carried out at the National Center for Electron Microscopy (NCEM) on an FEI Tecnai-F20 STEM equipped with a monochromator, which allows us to image small objects with high special resolution (~0.14nm) and simultaneously perform spectroscopy with high energy resolution (~0.15ev). This capability is a necessity to study transition metal related perovskite structures, where subtle changes in the atomic arrangement or distortion in the bond angles can lead to dramatic changes in the physical properties.

Fig.1 shows the Z-contrast images of YVO_3, $SrVO_3$ and $PbVO_3$ thin films and the interfaces. In contrast to $SrVO_3$ with a cubic structure, $PbVO_3$ films show a strong structural distortion along the c-axis and its c/a ratio was calculated to be 1.31 from diffraction. The bonding and valence states are studied here by investigating the fine structures of vanadium $L_{2,3}$ and oxygen K edges. To quantify the valence states of vanadium in each sample, EELS also have been performed on binary vanadium oxides under the same microscope condition. Fig.2 shows the EELS spectra from the standard binary oxides and from $SrVO_3$ and $PbVO_3$ films. Detailed quantification of vanadium valence states and electronic structures in the films and at the interfaces will be presented and the comparison with other vanadium perovskites will be discussed.

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[6] This research was performed at the National Center for Electron Microscopy and supported by the Department of Energy (DOE) under Contract No. DE-FG02-03ER46057, DE-AC03-76SF00098 and DE-AC02-05CH11231.

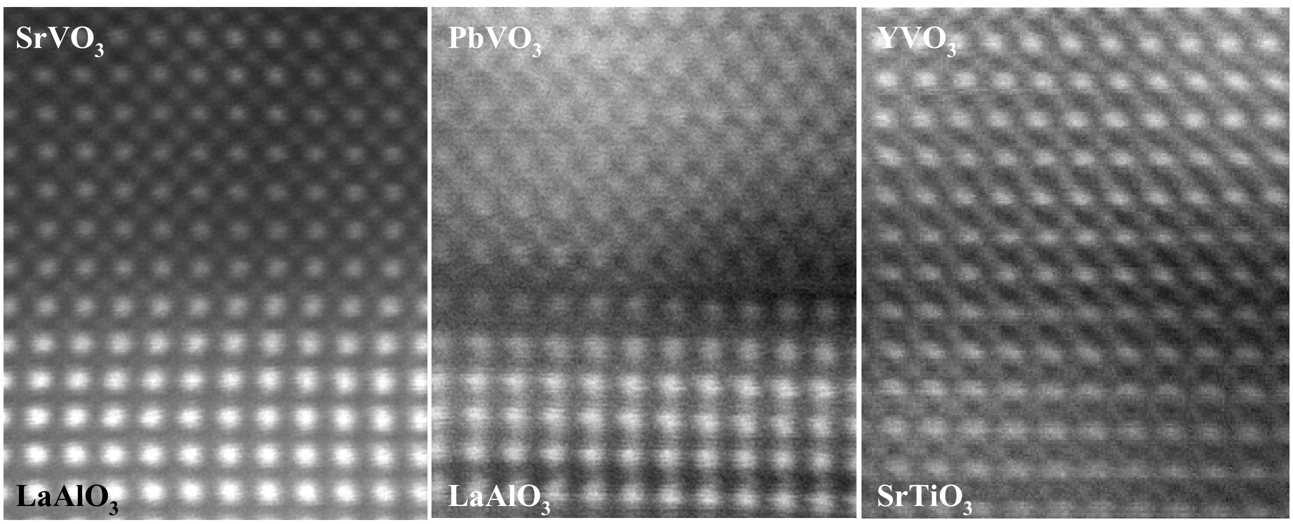

Fig.1. Z-contrast images of $SrVO_3$, $PbVO_3$ and YVO_3 thin films and their interfaces with the substrates.

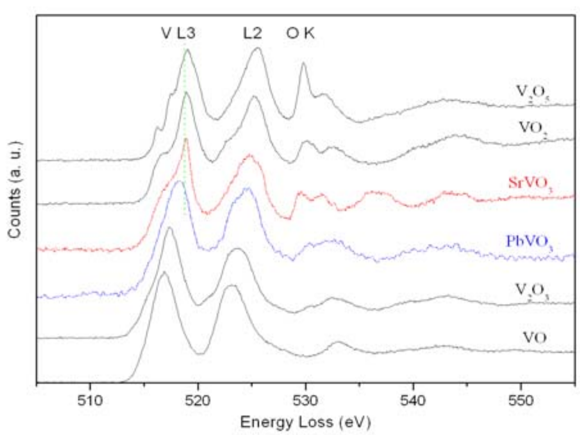

Fig.2. Vanadium L and oxygen K edges from binary vanadium oxides, $SrVO_3$ and $PbVO_3$ thin films.

https://doi.org/10.1017/S1431927606068255 Published online by Cambridge University Press