Beamline 9.3.2

Chemical and Materials Science, Circular Dichroism, Spin Resolution

A study of thermal stability of tungestophosphoric acid, $H_3PW_{12}O_{40}$, by XPS, XANES, hexane cracking, x-ray diffraction and IR spectroscopy

Jalil, P.A., M. Faiz, N. Tabet, N. Hamdan, Z. Hussain

Determination of formal oxidation state of Co in MBE-grown co-doped TiO_2(001) anatase epitaxial films by x-ray absorption spectroscopy

Chambers, S.A., T. Droubay, S. Thevuthasan, N.H. Hamdan

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Turko, B., M. Press, A.W. Kay, M. West, J.E. Katz, H. Spieler, Z. Hussain, C.S. Fadley, B. Ludewigt, J.-M. Bussat, P. Denes, H. von der Lippe, G. Meddler, G. Zizka, G. Lebedev, M. Mellon, T. Wiell

High resolution XPS investigation of oxide layer growth on Ge substrates

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Surface investigations of tungestophosphoric acid, $H_3PW_{12}O_{40}$, supported on MCM-41 mesoporous silica catalyst

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Valence band photoemission from pure and Sr diffused single crystal anatase TiO_2(001) surfaces

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A Study of Thermal Stability of Tungestophosphoric Acid, $H_3PW_{12}O_{40}$, by XPS, XANES, Hexane Cracking, X-Ray Diffraction and IR Spectroscopy

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Abstract

Tungestophosphoric acid (HPW) is considered as a super acid in a heteropoly acid series that has a Keggin type structure. Heteropoly acids have many industrial applications. It could be used as homogeneous or heterogeneous catalyst. Hence surface characterization is important to understand the reactions that occur on the surface, for example alkylation of aromatics.

Although some studies showed that HPW is a stable molecule up to 600 ºC, our work suggests that HPW starts loosing stability at temperature as low as 200 ºC. High resolution XPS analysis showed a shift of the W 4f peak towards the higher binding energies after heating the acid at 200 ºC and 400 ºC. In addition, the O 1s peak was shifted towards the lower binding energy that suggests the formation of higher oxidation states of tungsten in the Keggin structure.

Another important feature is that the P 2p peak was not detected at 100 ºC but was clearly observed after heating the acid under air at 200ºC and 400 ºC. This could be explained by the segregation of phosphorous atoms from the center of the HPW molecule to the surface. This means that the structure of the acid molecules on the surface is destroyed, which decreases their chemical stability.

Detailed infrared spectroscopic investigation of the HPW as a function of temperature showed a gradual increase in absorbance of the W-O-W corner shared vibration relative to the absorbance of the other bands. However, the features of the spectra and the absorbance of all the other bands were not changed. This indicates that the symmetry, and hence the stability, of the molecule was decreased upon heating.

Hexane cracking, a surface reaction, was used to investigate the acidity of the surface of the HPW. It was found that the catalyst deactivates completely after 12 minutes at 300 ºC. Also no hexane cracking occurred when the acid was heated at 350 ºC for 12 hours prior to reaction. This could be explained by the destruction of the surface due to heat and/or chemical reaction.

X-ray absorption near edge structures (XANES) of W N_3-edge and O K-edge of the HPW were also investigated as a function of temperature. The results will be discussed.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Determination of Formal Oxidation State of Co in MBE-Grown Co-doped TiO_2(001) Anatase Epitaxial Films by X-ray Absorption Spectroscopy

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INTRODUCTION

Diluted magnetic semiconductors (DMS) consist of nonmagnetic semiconducting materials doped with a few atomic percent of impurity magnetic cations. Magnetic coupling occurs by virtue of exchange interactions between the magnetic spins and free carriers in the semiconductor. The interaction can occur via *p-d* or *d-d* exchange, and can lead to antiferromagnetic or ferromagnetic coupling, depending on the concentration and the local structural environment of the magnetic impurity. DMS materials grown as thin epitaxial films can be used as spin injectors for semiconductor heterostructures, provided they are ferromagnetic.

Virtually all conventional DMS materials exhibit Curie temperatures of ~100K or less and must be *p*-type, which means that the exchange interaction leading to ferromagnetic behavior is hole mediated. Most of the effort expended to date on understanding the crystal growth and properties of thin-film DMS materials has focused on Mn-doped II-VI, III-V, and Group IV semiconductors.[1-4] Relatively little effort has gone into the investigation of "nontraditional" semiconductors, such as semiconducting oxides, to see if they are more robust magnetically. However, one such oxide - Co-doped TiO_2 anatase ($Co_xTi_{1-x}O_2$) - has recently been discovered to be the most magnetically robust DMS with regard to magnetic moment at saturation, coercivity, remanence, and Curie temperature.[5] Indeed, it is one of the very few DMS materials demonstrated to exhibit ferromagnetic behavior above 300K. In addition, it has been shown that the material can be grown epitaxially by both pulsed laser deposition (PLD)[6] and oxygen plasma assisted molecular beam epitaxy (OPA-MBE)[5] on $SrTiO_3$(001) and $LaAlO_3$(001). However, the resulting magnetic properties differed considerably for the two growth methods, with significantly better properties exhibited by OPA-MBE grown material.

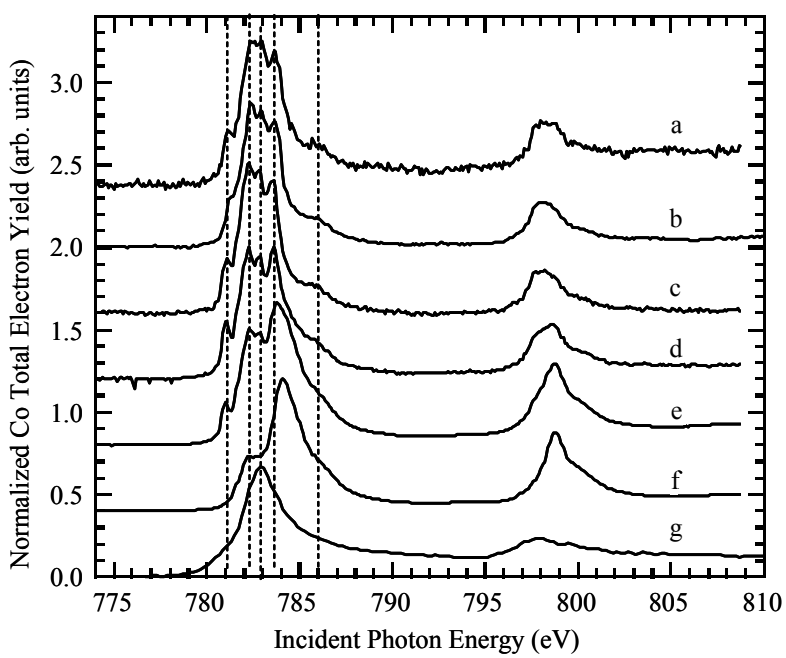
In order to understand the mechanism of magnetism in this fascinating material, it is essential to know the charge state of the magnetic cation (Co), and the doping type. We have utilized Co L-edge x-ray absorption spectroscopy (XAS) at beamline 9.3.2 to determine the Co charge state.

EXPERIMENT

Epitaxial $Co_xTi_{1-x}O_{2-x}$ films of high structural quality were grown by OPA-MBE on $LaAlO_3$(001)[7] using a system at PNNL described in detail elsewhere.[8] The resulting samples were then transferred through air to beamline 9.3.2 and XAS measurements were made in total electron yield mode at the Co L-edge, Ti L-edge, and O K-edge. X-ray absorption near-edge spectra (XANES) were also recorded for several Co standards for comparison purposes. No surface cleaning was done, as the distribution of Co has been shown to be strongly modified by post-growth annealing at the temperatures required to rid the surface of carbon, or remove sputter damage.

RESULTS

We show in Fig. 1 Co L-edge XAS data for three films with different Co mole fractions (x) (Fig. 1a-c), and for standards containing Co in different oxidation states and local structural environments (Fig. 1d-g). The $CoTiO_3$ standard was a powder, CoO was a (001)-oriented bulk single crystal, γ-Co_2O_3 was a 100 nm thick (001)-oriented epitaxial film grown on MgO(001) at PNNL, and the Co metal standard was a polycrystalline film evaporated *in situ* in the XAS chamber. Comparison of all film spectra with those for the standards reveals a good fit with both $CoTiO_3$ and CoO, which both contain Co^{+2}, but a very poor fit for both γ-Co_2O_3, which contains Co^{+3}, and for Co metal. The fit to $CoTiO_3$ is better than that to CoO. However, there is some similarity between the reference spectra for CoO and γ-Co_2O_3, particularly in the vicinity of the feature at 784 eV. This result indicates that there may be some Co^{+3} in the CoO single crystal. The very high degree of similarity between the spectra for the Co-doped anatase films and the $CoTiO_3$ standard establishes that Co in the former is in the +2 formal oxidation state. Interestingly, using the Co evaporation rate and oxygen plasma beam intensity we have used for the growth of $Co_xTi_{1-x}O_{2-x}$ result in the epitaxial growth of metastable γ-Co_2O_3 on MgO(001). Therefore, the anatase lattice stabilizes the formation of Co(II), even though the conditions would result in Co(III) formation if pure Co oxide were allowed to grow under comparable



conditions.

Fig. 1 Co L-edge XAS for 20 nm thick films of epitaxial $Co_xTi_{1-x}O_{2-x}$ on $LaAlO_3$(001): (a) x = 0.01, (b) x = 0.06, (c) x = 0.08. Also shown are spectra for reference compounds containing Co in different formal oxidation states: (d) $CoTiO_3$, (e) CoO, (f) γ-Co_2O_3, and (g) Co metal.

SIGNIFICANCE

Ion channeling measurements conducted at PNNL reveals that Co substitutes for Ti in the anatase lattice. Furthermore, Hall effect measurements carried out at PNNL show that these films are *n*-type semiconductors as grown, despite the fact that no intentional *n*-type doping was carried out. The origin of the *n*-type doping may have to do with the presence of H in the film,

which has been detected by ^{19}F nuclear reaction analysis at PNNL at a concentration that is of the same order of magnitude as that of the free carriers – 10^{19} to 10^{20} cm^{-3}. H may be the direct dopant, as occurs in *n*-ZnO.[9] Alternatively, H_2, which is present in the growth chamber at a very low partial pressure, may partially reduce lattice oxygen during growth to produce OH and a free donor electron according to the reaction $O^{-2}_{(lattice)} + (1/2)H_2 \rightarrow OH^{-}_{(lattice)} + e^{-}$. This phenomenon is currently under more detailed investigation.

It thus appears that Co-doped anatase TiO_2 is ferromagnetic by virtue of *electron* mediated exchange interaction between Co^{+2} cations that substitute for Ti^{+4} in the lattice. In order to maintain charge neutrality, each substitutional Co^{+2} must be accompanied by an O^{-2} vacancy. However, such vacancies are uncharged and therefore do not contribute any donor electrons. In fact, *n*-type semiconducting behavior and Co substitution are independent phenomena; some highly resistive films are nonmagnetic despite having several at. % Co. Indeed, the magnetization depends as much on the free carrier concentration as on the presence of substitutional Co, as expected for a DMS.

Significantly, virtually all other known DMS materials are ferromagnetic by virtue of *hole* mediated exchange interaction, which has been thought to be the stronger interaction.[10] Therefore, Co-doped TiO_2 anatase is a highly unusual and potentially very important DMS in that it exhibits strong electron mediated exchange interaction at temperatures of at least 500K. No other known DMS exhibits these properties.

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The work was funded by a Laboratory Directed Research and Development grant associated with the PNNL Nanoscience and Technology Initiative, and by DOE BES Materials Science.

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Development of a GHz-Rate Detector for Synchrotron Radiation Research

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INTRODUCTION

It has by now become obvious that the brightness of third-generation synchrotron radiation sources often exceeds the capabilities of the end-station detector systems to adequately handle the electron or photon fluxes resulting from a given experiment, thus preventing both the fullest utilization of the radiation and the carrying out of certain new types of experiments readily, if at all. Detector non-linearity is one problem that has been encountered [1], but there are many other examples for which beamline or spectrometer throughput must be decreased to prevent high countrate saturation, or the number of energy or angular channels that can be counted simultaneously severely limits a given experiment [2]. In recognition of this, a national-level initiative in detector development has been proposed by the multi-institutional "DetectorSync" group [2].

As a first example of what can be accomplished with advanced detector technology, a project to develop an ultrahigh-speed one-dimensional detector for electrons and vuv/x-ray photons is underway at the ALS.

DESIGN PHILOSOPHY AND FIRST TEST RESULTS

This project takes advantage of unique expertise at LBNL for detector development in high-energy and nuclear physics, and involves the custom design and fabrication of application-specific integrated circuits (ASICs). The final goal is a 768-channel detector with 50 micron spacing between channels and a maximum linear countrate per channel of over 2 megaherz. The overall countrate will thus be in the 2 GHz range, and approximately 100 times faster than any other present one-dimensional or two-dimensional detector, with significantly improved spatial resolution as well compared to other existing detectors. First applications will be in electron spectroscopy, but others in x-ray absorption and x-ray emission spectroscopy are expected to follow.

A first prototype of this detector is shown in Fig. 1(a). Based on 12 pairs of 64-channel ASICs (an existing high-energy preamplifier chip (SDC) and a specially-designed buffered counter (DBC)), this detector has already demonstrated the ability to take spectra in a Scienta electron spectrometer located at the ALS (Fig. 2(a)), to resolve channels with a FWHM of 75 microns (Fig. 2(b)), and to count linearly at up to 1.0 GHz overall (Fig. 2(c)) [3].

Based on this experience, a next-generation detector with significant improvements in all elements from power supplies to ASICs to data acquisition is presently under development, with an expected completion date of late 2002. This will use 6 pairs of 128-channel ASICs (a newer high-energy preamplifier chip (CAFÉ-M) and a specially-designed buffer counter (BMC)), with optical coupling between detector and control/counting electronics to minimize noise and transients. The completion date for this project is estimated to be late 2002.

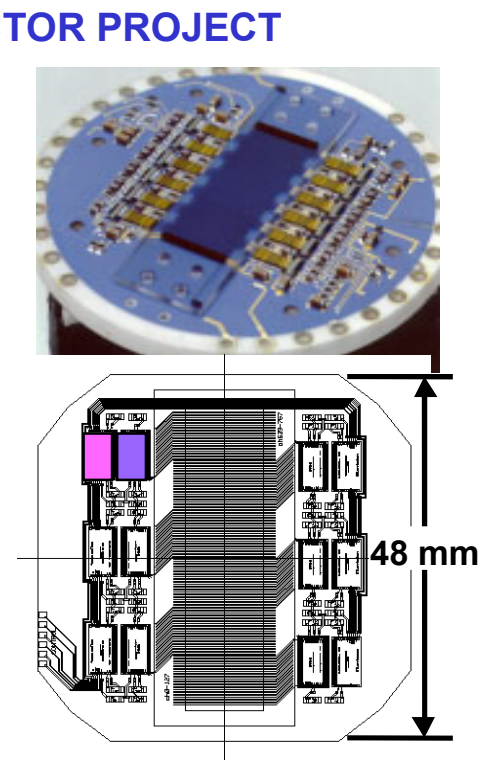

Figure 1--(a) Basic characteristics of the prototype GHz-rate detector developed as the first stage of this project, together with a photo of the ceramic substrate with 12 preamp-plus-counter chipsets mounted on it. The microchannel plates are not yet installed. (b) Basic characteristics of the next-generation detection now being designed and fabricated, together with a layour of its 6 chipsets and an indication of its size.

CONCLUSIONS

A prototype one-dimensional electron and photon detector operating linearly up to the GHz countrate level and with a resolution of 75 microns over 768 channels has been successfully developed and tested. An improved version of this detector is under development, with the same resolution and number of channels, but improved performance, programmability, and robustness in general user environments relative to the prototype. The next-generation detector should find use in several areas of synchrotron radiation research.

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[2] Local participants in the DetectorSync initiative include A. Thompson, H.A. Padmore, and C.S. Fadley, and the group's website is at--http://www-esg.lbl.gov/esg/meetings/detectorsync/index.html, with a more detailed white paper on detector needs also downloadable from this source.
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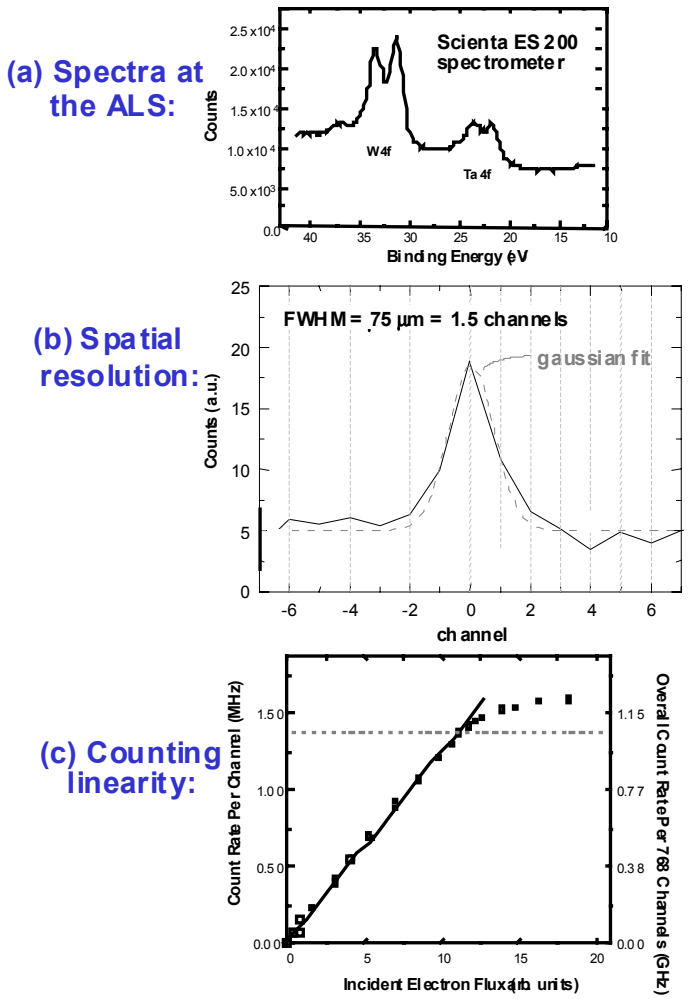

Figure 2--Test data from the first prototype detector shown in Fig. 1(a). (a) Test spectra obtained with the detector mounted in a Scienta SES 200 spectrometer at ALS beamline 9.3.2. (b) Spatial resolution determination via a collimated electron beam source. Each channel is 50 microns. (c) Counting linearity per channel (ledt scale) and over all channels (right scale) as determined with an electron gun.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, under Contract No. DE-AC03-76SF00098..

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High Resolution XPS investigation of Oxide layer grown on Ge substrates

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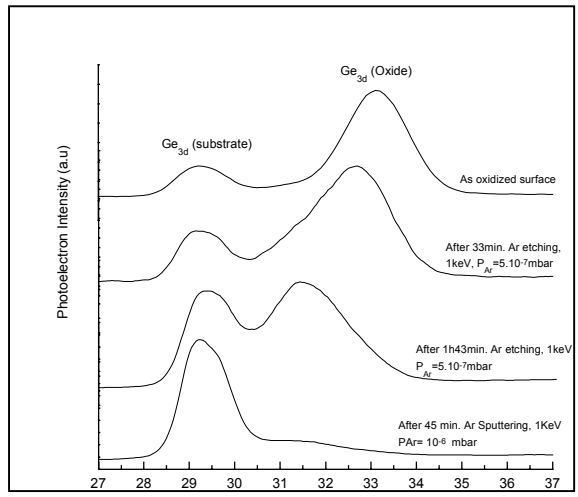
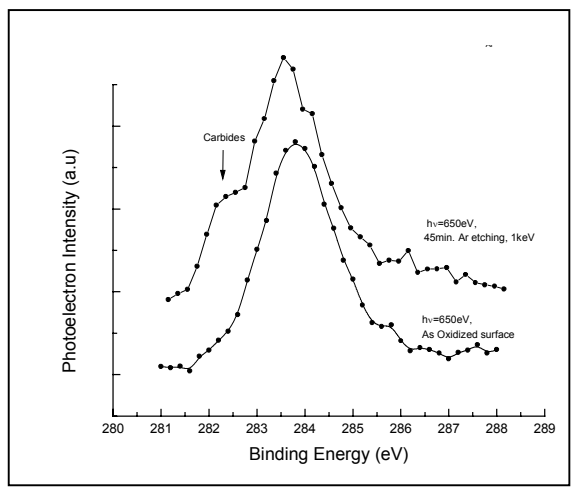
Abstract

We present an XPS study of thin oxide layers grown by thermal oxidation of germanium substrate at T = 380 ºC, under 400 mTorr of dry air. The samples were mechanically then chemically polished prior to the heat treatments. Ge3d, O1s and C1s lines were recorded after successive cycles of ion etching at low Argon pressure. The Ge3d spectra showed a shift of the oxidized germanium peak from 33.2 eV to 31.5eV binding energy while the peak corresponding to the non-oxidized germanium atoms of the substrate remains fixed at 29.2eV. The analysis of a GeO_2 amorphous sample showed no shift in the binding energy of the Ge peaks. The 31.5 eV binding energy peak observed during the analysis of the oxide layer grown on germanium substrate was attributed to the formation of a stable GeO phase under argon bombardment. In addition, the results showed the emergence of a carbon peak of low binding energy (E_b=282.3eV) at the interface Ge/GeO_2. This peak was attributed to the formation of carbides during the heat treatment.





This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Surface Investigations of Tungestophosphoric Acid, $H_3PW_{12}O_{40}$, Supported on MCM-41 Mesoporous Silica Catalyst

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Abstract

A catalyst system of large pore size, such as supported acid on MCM-41, could be more suitable for reactions involving bulk size molecules. The pore size could range from 2.0 to 50 nm. All-silica MCM-41 is not acidic material. However, an acid could be impregnated in MCM-41 to make the surface acidic. Due to its super acidity, tungestophosphoric acid (HPW) was chosen to be impregnated in MCM-41. The surface properties and the stability of the new system are important factors to know for determining what kind of reactions could be used with these systems.

High resolution XPS showed a shift of the W 4f peak towards the higher binding energy after heating the acid under air at 200 ºC and 400 ºC. This shift was associated with a decrease of the O 1s binding energy. These results suggest the formation of higher oxidation states of the W atom in the Keggin structure of the HPW acid. In addition, the W $4f_{7/2}$ and W $4f_{5/2}$ spin-orbit split doublet was not resolved as a result of a drastic broadening of the peaks. This indicates that the impregnation destabilizes the supported acid that may affect its chemical activity.

X-ray absorption near edge structures (XANES) of the W N_3-edge, O K-edge and Si $L_{2,3}$-edge were also investigated as a function of temperature. The results will be discussed.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Valence band photoemission from pure and Sr diffused single crystal anatase TiO_2(001) surfaces

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INTRODUCTION

Titanium oxide is one of the most extensively studied transition metal oxides because of its availability and its wide use in a variety of technological applications. A large number of electronic, geometric , and catalytic studies of commercially available high-quality single crystal titanium oxide surfaces have been reported in the literature [1-3]. In contrast, although the anatase polymorph of titanium oxide show s a number of interesting chemical behaviors, including superior photocatalytic activities in comparison to rutile titanium oxide [4-7], investigations of high-quality anatase titanium dioxide are limited in the literature due primarily to the lack of availability of well-ordered single crystals.

Recently, single crystal anatase TiO_2(001) thin films were successfully grown on (001) surfaces of $SrTiO_3$ and $LaAlO_3$ surfaces using molecular beam epitaxy [8-10]. Surface structural study of these high quality single crystal films using angle-resolved mass spectroscopy of recoiled ions (AR-MSRI) [8] has identified a two domain (1x4) reconstruction on the anatase TiO_2(001) surface. It was suggested that the anatase (001) surface reconstructs to form a microfaceted surface that exposes (103) and (-103) surface planes. A missing oxygen row model was proposed from a low energy electron diffraction study, where the authors suggested a reduced surface was likely [9]. A subsequent scanning tunneling microscopy (STM) study confirmed the existence of the two domain (1x4) surface reconstruction of anatase (001) surface [10]. However, the authors described this reconstruction in terms of added and missing rows at the surface, which is slightly different from the previous two studies. A recent theoretical study by first principle density functional calculations proposed a fourth model, which is based on the replacement of bridging oxygen rows with rows of TiO_3 units and thus does not contain any reduced Ti^{3+} cation [11], consistent with x-ray photoemission (XPS) data [12]. In two of the experimental studies, core level x-ray photoelectron spectroscopy was used to investigate the electronic structure in the surface region and the authors did not observe any state due to reduced Ti^{3+} cation. Since core level XPS using conventional Al and Mg x-ray sources is sensitive to many layers in the surface region, it is difficult to obtain chemical properties of only the top most surface layer. Conventionally, valence band photoemission has been extensively used to address the issues related to the surface layer including the existence of surface states.

In a recent valence band investigation of single crystal anatase TiO_2 (101) surfaces using Al Kα x-rays, it was reported that the VB of anatase shows characteristics similar to those reported for the rutile polymorph [13]. In addition, no indications of intrinsic surface states were observed in this study. Although no intrinsic surface states were reported for clean un-reconstructed (101) surfaces, intrinsic surface states may exist for the (001) surface because of its two domain (1x4) reconstruction. In order to investigate this, we have carried out a series of valence band photoemission measurements at the Advanced Light Source (ALS) using high quality single

crystal anatase TiO_2(001) films grown on $SrTiO_3$(001) substrates. We also investigated the effects of Sr diffusion in the VB photoemission from these samples.

EXPERIMENT

The growth of anatase TiO_2(001) were carried out in an oxygen plasma assisted molecular beam epitaxial system (OPA MBE) described elsewhere [14]. Pure single crystal 1cmx1cmx1mm $SrTiO_3$(001) substrates were used in this study. Two clean Ta clips were used to hold the sample on the sample holder and a pair of thermocouples were fastened to the sample holder under one clip near a corner of the sample for temperature measurements. Before each growth, the substrates were cleaned using the oxygen plasma at a sample temperature of 950 K at P_{O2} = 2.0×10^{-5} Torr. The growth temperature was maintained at 875 K to avoid Sr diffusion into the film at high temperatures. During the growth, the Ti flux was evaporated from an e-gun emitter source in the presence of the oxygen plasma. In addition, oxygen pressure in the chamber was maintained at 1.5×10^{-5} Torr. In-situ XPS and ex-situ Rutherford backscattering spectrometry (RBS) along with x-ray diffraction was used to characterize these films. After these characterizations at the Environmental Molecular Sciences Laboratory, the samples were brought to the Advanced Light Source (ALS) for the valence band photoemission measurements at beam line 9.3.2. The end station at this beam line is equipped with Scienta SES 100 hemispherical analyzer for collection of photoelectron spectra, along with a five-axis sample manipulator and in-situ sample cleaning capabilities. The samples were cleaned and ordered by cycles of light 500 eV Ar^+ ion sputtering, annealing in oxygen at a pressure of 1×10^{-6} Torr and a temperature of 800 K.

RESULTS

Fig. 1 shows the valence band (VB) spectrum from a clean (1x4) reconstructed anatse TiO_2(001) surface. A photon energy of 80 eV was used to collect the photoelectrons at normal emission. This spectrum is similar to the spectrum reported for anatase TiO_2(101) [13] and it shows a wide O 2p feature, which is similar to the O 2p feature from the rutile TiO2 [15-17], centered around

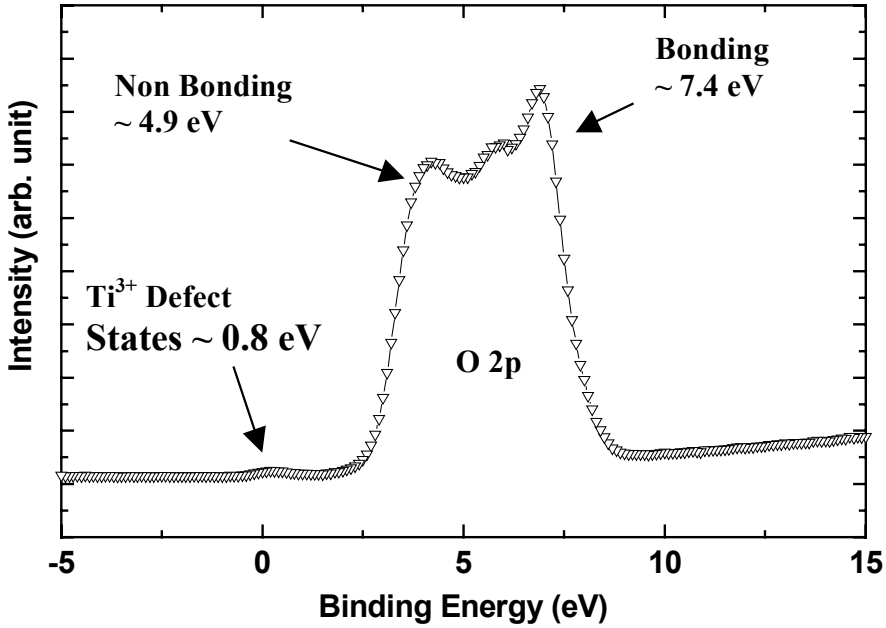

Fig. 1: Valence band spectrum from clean (1x4) anatase TiO_2(001) surface

6.5 eV. The width of this feature is about 4.7 eV and it consists of photoelectron contribution from π bonding (non bonding, peak at ~ 4.9 eV) and σ bonding (bonding, peak at ~ 7.4 eV) O 2p-Ti 3d orbitals. The band gap is about 3.1 eV and the feature at about 0.8 eV from the Fermi level is due to Ti^{3+} defect states related to the remnant of sputtered defects, which were not completely healed during the annealing in oxygen. No surface state associated with two domain (1x4) surface reconstruction was visible in the spectrum.

During the experiments, several mild sputtering and vacuum and oxygen annealing cycles were carried out to enhance Sr diffusion to the surface of the film. At the end of these processing cycles, about 1-2% of Sr was accumulated at the surface. These surfaces still showed a (1x4) surface reconstruction and VB spectra were collected from Sr diffused surfaces at normal and glancing emission. No differences between these spectra and the VB spectra from the clean surface were observed. The absence of any change in the VB spectra within our experimental uncertainties suggests that the Sr diffusion in small amounts did not alter the electronic structure of the anatase (001) surface.

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This work was supported by the LDRD program of Pacific Northwest National Laboratory.

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