# ACS APPLIED MATERIALS & INTERFACES

Cite This: ACS Appl. Mater. Interfaces 2019, 11, 21720–21726

www.acsami.org

# Electron Doping BaZrO<sub>3</sub> via Topochemical Reduction

Thomas Orvis,<sup>†</sup> Mythili Surendran,<sup>†</sup> Yang Liu,<sup>†</sup> Shanyuan Niu,<sup>†</sup> Shin Muramoto,<sup>‡</sup> Alexander J. Grutter,<sup>‡</sup> and Jayakanth Ravichandran\*<sup>,†,§</sup>

<sup>†</sup>Mork Family Department of Chemical Engineering and Materials Science and <sup>§</sup>Ming Hsieh Department of Electrical Engineering, University of Southern California, Los Angeles, California 90089, United States

<sup>\*</sup>National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, United States

Supporting Information

ABSTRACT: We report the topochemical reduction of epitaxial thin films of the cubic perovskite BaZrO<sub>3</sub>. Reduction with calcium hydride yields n-type conductivity in the films, despite the wide band gap and low electron affinity of the parent material. X-ray diffraction studies show concurrent loss of out-of-plane texture with stronger reducing conditions. Temperature-dependent transport studies on reduced films show insulating behavior (decreasing resistivity with increasing temperature) with a combination of thermally activated and variable-range hopping transport mechanisms. Time-dependent conductivity studies show that the films are stable over short periods, with chemical changes over the course of weeks leading to an increase in electrical resistance.



Neutron reflectivity and secondary ion mass spectrometry indicate that the source of the carriers is most likely hydrogen incorporated from the reducing agent occupying oxygen vacancies and/or interstitial sites. Our studies introduce topochemical reduction as a viable pathway to electron-dope and meta-stabilize low electron affinity and work function materials.

KEYWORDS: barium zirconate, pulsed laser deposition, low electron affinity, hydrogen, complex oxide, perovskite

# ■ INTRODUCTION

BaZrO<sub>3</sub> (BZO) is a cubic perovskite oxide broadly studied for diverse applications such as in catalysis,<sup>1</sup> in thermal barrier coatings,<sup>2</sup> and as an electrolyte in solid oxide fuel cells.<sup>3</sup> BZO's high degree of chemical stability makes it an attractive candidate for utilization in harsh environments. Some of its appealing features are wide band gap (5.3 eV),<sup>4</sup> ease of doping,<sup>5,6</sup> and low electron affinity.<sup>4,7,8</sup> Electron affinity and work function play a critical role in electrochemical reactions such as oxygen reduction<sup>9</sup> and CO oxidation,<sup>10</sup> the electrical properties of heterojunctions in complex oxides<sup>11</sup> and nitrides,<sup>12</sup> and the efficiency of electron emission and photoemission devices.<sup>12</sup> Frequently, the low electron affinity or work function of the materials is beneficial to drive these processes. Hence, low electron affinity materials, which are stable under adverse conditions, can find a wide variety of applications. Unfortunately, typical low electron affinity materials tend to be unstable metals susceptible to rapid oxidation or stable insulators, which have a large band gap, causing significant difficulties in creating itinerant carriers. Aliovalent doping or alloying in these wide-band-gap materials is thermodynamically unfavorable as the induced carriers are unstable and reactive, which results in surface and bulk compensation reactions to lower their energy. Therefore, the kinetic stabilization of electron-doped low electron affinity transition metal oxides such as BZO can be a viable path to meta-stabilize these phases and overcome this challenge.

The wide band gap and low electron affinity of BZO contribute to its high stability and low reactivity but simultaneously impede efforts to introduce itinerant electrons. Typical aliovalent substitutions replace an atom of parent material with a foreign species, such as La for Ba or Y for Zr in BZO, and/or substituting a proton on an oxygen site. Most substitution efforts have centered on achieving high proton conductivity with high transference number (low electronic conductivity).<sup>3</sup> Compared to perovskite titanates such as SrTiO<sub>3</sub>, exchanging the B-site cation selection in the ABO<sub>3</sub> perovskite structure from Ti to Zr considerably lowers the electron affinity due to the higher relative energy of the Zr dband as compared to the Ti d-band.<sup>7</sup> Hence, if one were to apply the same doping methods used for SrTiO<sub>3</sub> to BZO, we would observe the formation of compensating point defects such as Ba or Zr vacancies, or the stabilization of mobile protons, instead of the desired electron doping. Specifically, the locations of the conduction band, valence band, and charge neutrality level in BZO, and similar wide-band-gap low electron affinity materials, make traditional donor doping extremely difficult if not impossible.<sup>6</sup> One way to overcome these thermodynamic limitations is to use kinetically controlled doping methods to avoid compensation reactions. For example, low-temperature topochemical reactions leverage

Received: April 11, 2019 Accepted: May 20, 2019 Published: May 22, 2019

the strong reducing or oxidizing character of a reactant to create large, non-equilibrium, quantities of oxygen vacancies or proton occupied oxygen vacancy sites.<sup>13</sup> CaH<sub>2</sub>, LiH, and NaH have been used to reduce numerous transition metal oxide perovskites, such as nickelates,<sup>14,15</sup> manganites,<sup>16,17</sup> ferrites,<sup>18,19</sup> and titanates,<sup>13,20</sup> thereby creating metastable compounds with a range of novel structures and, often ordered, oxygen deficiencies.<sup>21</sup> To the best of our knowledge, this reduction method has not been used on zirconate perovskites, though it has been successful in reducing and proton-doping titanate perovskites, where bulk electron doping methods have already been successful.<sup>20,22,23</sup>

During doping, charge compensation must occur to maintain net charge neutrality, and the nature of this charge compensation will determine the electronic properties of the material. In perovskite titanates, compensation is achieved by reducing Ti<sup>4+</sup> to Ti<sup>3+</sup>. Though less common than its Ti<sup>3+</sup> counterpart, Zr<sup>3+</sup> is stable in compounds such as ZrN and, potentially, ZrH<sub>3</sub>.<sup>24</sup> However, although BZO band structure calculations suggest that BaZrO2.5 will be a metal with the Fermi level in the Zr 4d band, the oxygen vacancies have a positive energy of formation.<sup>25</sup> Finally, past studies have shown the stabilization of an oxyhydride in BaTiO<sub>3</sub>, which also produced electronic carriers.<sup>13,26</sup> Therefore, investigating the reduction of BZO, either by introducing oxygen vacancies or incorporating hydrogen, will provide insight into the mechanisms, properties, and viability of reducing a whole class of complex oxide perovskites.

#### RESULTS AND DISCUSSION

We deposited BZO thin films using pulsed laser deposition (PLD) on DyScO<sub>3</sub> (110) (DSO) and (LaA- $1O_3$ )<sub>0.3</sub>(Sr<sub>2</sub>TaAlO<sub>6</sub>)<sub>0.7</sub> (111) (LSAT) single crystal substrates purchased from Crystec GmbH. The growth target was phasepure BZO densified to >95% theoretical density via spark plasma sintering. The films were grown epitaxially in layer-bylayer growth mode, with thickness and surface structural quality verified by in situ and real-time monitoring of the reflection high energy electron diffraction (RHEED) pattern, shown in Figure S1. We verified the epitaxial quality and thickness of the as-grown films and compared them to reduced films with various thin film X-ray diffraction (XRD) measurements such as  $2\theta - \theta$ , rocking curve, X-ray reflectivity, and reciprocal space mapping (RSM). Utilizing established methods for thin films, the as-grown films were topochemically reduced with CaH<sub>2</sub> in evacuated quartz ampoules.<sup>20</sup> Because of the native low electron affinity of BZO, the parent compound, oxygen-vacancy reduction is thermodynamically unfavorable. Hence, we resorted to higher temperatures than those typically used for reducing similar perovskites.<sup>21</sup> As-grown films of BZO were transparent, but the reduction process turned the films opaque and black in color. This change in the color and absorption characteristics are consistent with past studies<sup>20</sup> and suggest possible introduction of free carriers. Vacuum-reduced BZO films, under similar temperature and vacuum conditions used to prepare rBZO, did not exhibit any measurable electrical conductivity. Postreduction XRD measurements identical to those performed on the as-grown films were conducted to identify changes in the structure of reduced BZO, shown in Figure 1. However, our initial attempts to reduce the films at temperatures below 500 °C were unsuccessful without measurable conductivity (4-wire resistance > 200 M $\Omega$ ) and largely unchanged XRD pattern. Upon



**Figure 1.** Thin-film XRD pattern of a 100 nm thick BZO film on  $DyScO_3$  substrate before and after topochemical reduction at various temperatures. The quality of the unreduced film is demonstrated by the prominent Laue fringes, which verify the reported thickness, as well as the narrow rocking curve full width half maximum of 0.034°, shown in comparison to the substrate in inset (a). The four-point resistance of the film decreases with the intensity of the BZO 002 peak as the reduction temperature increases, until a critical point at which the film loses texture. The color of the film also changes from translucent to dark with hydride treatment as shown in inset (b).

increasing the reduction temperature to 500 °C and baking for 72 h, we observed measurable conductivity (4-wire resistance  $\approx$  100 M $\Omega$ ) and a decrease in the intensity of the out-of-plane 002 peak. However, the stability of the 500 °C-reduced BZO (rBZO) film was poor in air and resistance increased to unmeasurable values within 24 h. We observed that successive reductions at increasing temperatures for the same duration resulted in improved conduction and stability in air but were accompanied by progressive loss of epitaxial texture as seen in the decrease of *d*-spacing of 002 reflection of the rBZO films with successively higher temperature reduction. This shift suggests c-axis compression arising from the induced carriers, or structural and chemical changes due to reduction-induced defects, especially point defects. After reduction at 575 °C for 72 h, we observed a complete loss of texture, signifying that the film became either amorphous or polycrystalline. Our extensive efforts to identify the residual polycrystalline phases using powder diffraction studies failed. The presence of intense reflections from the substrate limited us from deriving conclusions about the crystallinity of the reduced films. Hence, we do not have sufficient evidence to confirm the exact structural state of the reduced films.

To gain insight into the structural impact of reduction on the BZO thin films, we performed RSM on two BZO films of different thicknesses grown on LSAT substrates, shown in Figure S2. Both films were relaxed in the as-grown state. The films were partially reduced simultaneously in order to mimic the film reduced at 550 °C shown in Figure 1, while maintaining sufficient surface smoothness and crystallinity to perform additional characterizations. Additional details are provided in the Supporting Information. RSM measurements on the reduced films were conducted to observe the structural changes in the films during the loss of out-of-plane texture. The 120 nm thick film exhibited c-axis compression and inplane (a- and b-axis) expansion during reduction with a marked decrease in the reflection intensity and peak broadening. We could not find the 103 reflection for the 20 nm film post-reduction. This behavior is similar to titanates albeit with a larger degree of disorder.<sup>20</sup> Note that the LSAT substrate 103 peak maximum location is unchanged for both films through the reduction process, demonstrating their stability. We also

grew BZO films on amorphous silica substrates purchased from MTI, yielding amorphous films as observed by RHEED. The resulting films had similar electrical conductivity as compared to the reduced epitaxial films after reduction at 650  $^{\circ}$ C for 120 h. However, the reduced amorphous films suffered from accelerated loss of conductivity possibly due to re-oxidation. This suggests that the structure of the as-grown film plays an important and complex role in the stability of the reduced films.

We performed low-temperature electrical transport measurements on two different series of rBZO films. The BZO films were grown on DSO and LSAT substrates, which have lattice mismatches of -5.5 and -7.8% with BZO, respectively. Both DSO and LSAT substrates show excellent stability during the topochemical reduction process.<sup>20</sup> To ensure that the substrates were not responsible for the measured conductivity, substrates identical to those used for the growths were reduced in the same ampoules together with the films used for transport measurements. The substrates alone did not conduct, but those deposited with BZO films did. Regardless of the substrate, the quality of the as-grown BZO films used for transport measurements was verified by thin film XRD, and loss of texture was likewise verified after reduction at 650 °C for 120 h.

We performed temperature-dependent resistivity measurements on films grown on both LSAT and DSO substrates, which are presented in Figure 2. Hall measurements on films



Figure 2. Resistivity, sheet carrier density, and carrier mobility versus temperature for rBZO thin films which all show insulator behavior. The thickness-dependent resistivity suggests that the oxidation process of the reduced films is also thickness-dependent. Dotted lines are a guide to the eye.

grown on LSAT substrates were used to deduce carrier density and mobility as shown in Figure 2. We observed insulating behavior in temperature-dependent resistivity measurements of the reduced films, regardless of thickness or substrate but with a measured room temperature conductivity more than 5 orders of magnitude greater than unreduced BZO films prepared in the same manner. The as-grown unreduced BZO films, as well as both reduced and unreduced DSO and LSAT substrates without BZO films, were resistive beyond the measurement capabilities of our equipment. We limited the reduced films' exposure to air as much as possible before conducting transport measurements.

The deduced sheet carrier densities from Hall measurements of the rBZO films grown on LSAT substrates were  $\sim 10^{16}$  cm<sup>-2</sup> for 40 and 80 nm films and  $\sim 10^{14}$  cm<sup>-2</sup> for 20 nm films. The calculated mobility values ( $\ll 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) from the studies were also low, very likely due to poor crystallinity of the reduced films. The apparent low temperature drop-off in carrier density can be attributed to freeze out of the carriers and the hopping nature of conduction, though it should be noted that the classical relationship between Hall coefficient and carrier concentration is no longer valid in the variablerange hopping transport regime. The carrier concentration of the 20 nm film is much lower than the thicker films likely due to the thickness-dependent re-oxidation process, discussed in further detail later. More importantly, a fundamental understanding of the system will be dependent on the mechanism responsible for generating carriers. In the case of Ba, Sr, and Ca titanates, reducing conditions are shown to create free carriers, and especially with hydride reduction processes, similar to our study, a combination of oxygen vacancies and introduction of hydrogen leads to free carriers.<sup>13,20,27</sup> In the case of zirconates, theoretical studies show that oxygen vacancies are deep donors, and H<sup>-</sup> occupying either an interstitial or oxygen vacancy site could act as a shallow donor.<sup>25,28</sup> We will discuss this further in the light of chemical analysis of these films.

To gain a more mechanistic understanding of the transport processes, we attempted to fit the electrical resistivity with well-known transport models.<sup>29</sup> The most common model for insulating behavior is activated transport, where the carriers are generated by thermal excitation from band-to-band or defectlevel-to-band excitations. This process follows the Arrhenius behavior governed by Boltzmann statistics

$$\rho = \rho_0 \, \mathrm{e}^{E_\mathrm{A}/k_\mathrm{B}T} \tag{1}$$

where  $\rho_0$  is a pre-exponential factor,  $E_A$  is the activation energy, and  $k_B$  is the Boltzmann constant. At low temperatures, variable-range hopping (VRH) conduction will take over, with the temperature-dependent resistivity given as

$$\rho \propto \mathrm{e}^{(T_0/T)^n} \tag{2}$$

with

$$T_0 = \frac{24 \cdot \alpha^3}{\pi \cdot k_{\rm B} \cdot N_{\mu}} \tag{3}$$

where *n* is dependent on the density of states at the Fermi level and equals 1/4 for disordered systems without Coulomb interaction. For two-dimensional systems with moderate density n = 1/3, and for a density of states at the Fermi level influenced by Coulomb interaction n = 1/2.<sup>30,31</sup> In the evaluation of  $T_0$ ,  $N_{\mu}$  is the density of localized states around chemical potential  $\mu$  (in volume and energy), and  $\alpha$  is the localization parameter, a description of the potential landscape in the region of the hopping sites.<sup>32</sup>

We fit the transport data to the thermal activation model (eq 1) and VRH model (eq 2) with the various values for *n*. We assumed that the activation model would be dominant at high temperatures and the VRH model at low temperatures, which was verified by the  $R^2$  value of the fits of each model in the respective regions. The  $R^2$  values of the thermal activation fits were calculated for temperature intervals from 300 K to (300 - 2N) K, with N = 1, 2, ..., 149, and the  $R^2$  values of the VRH

fits were calculated for temperature intervals from 2 K to (2 + 2N) K. We observed that Mott VRH provides the best fit at low temperatures with n = 1/4. The  $R^2$  values of the thermal activation and VRH fits for each temperature range were summed, such that a single  $R^2$  was representative of both fits with a transition from one to the other at a given temperature. The temperature at the peak of the summed  $R^2$  values was determined, indicating the best dual fit to the electronic transport data, and chosen to serve as a qualitative transition point (QTP) from one mode of transport to the other. The data with corresponding fits are shown in Figure 3, with the



**Figure 3.** Reduced BZO thin film resistivity data fit to the Mott variable-range hopping model (low temperature, blue) and thermal activation model (high temperature, red). The transition point between the two models was determined by selecting the temperature with the highest sum of  $R^2$  values for the two fits. Regardless, the data suggest that both conduction phenomena are present over the full temperature range measured, with a gradual shift in the dominant mode.

transition between models demarcated as a color change. The QTP for the rBZO samples is inversely related to sample thickness, providing further indication of inhomogeneity in the reduction process and time-dependent re-oxidation or other chemical changes. Regardless of the QTP value, conduction is the result of a combination of mechanisms over the temperature range observed, and the QTP simply reflects the relative weight of the mechanisms modeled. Additional tabulated transport coefficient values can be found in Table S1.

To observe the stability of the rBZO films grown on LSAT substrates, they were left in air with four-wire resistance measurements taken over time, shown in Figure 4. The resistance shows two distinct regions for the 40 and 80 nm samples: an initial short period (<3 days) of rapidly increasing resistance followed by a prolonged exponential time dependence (up to 60 days). The 20 nm sample instead shows two regions with varying time dependence, without the exponential behavior observed in the thicker films. The time evolution of resistance follows an exponential  $(e^t)$  time dependence in the beginning and then transitions to a power law  $(t^2)$ . The data clearly show that the chemical changes at work causing the increase in resistance are inadequately described by Fick's laws alone, for which the diffusion length shows a  $t^{1/2}$  dependence. A full understanding of the mechanism behind the time evolution of resistance requires the origin of the carrier generation and how the chemical species creating these carriers



**Figure 4.** Time-dependent four-wire resistance of rBZO thin films grown on LSAT substrates. The resistance shows two distinct regions of behavior, with an initial period loosely proportional to  $t^2$  and a later period proportional to  $e^t$ . A line fit of the 40 and 80 nm films between 10 and 60 days yields nearly identical slopes, indicating that the mode of resistance increase is common to both but not observed in the 20 nm film.

evolve in time, and is beyond the scope of the current study, requiring extensive time-dependent chemical analysis of the reduced films.

To shed light on the carrier generation mechanism, we need to understand the chemical changes in the film as a result of the reduction process. We performed neutron reflectivity on a 120 nm thick rBZO film grown on an LSAT substrate to probe the oxygen and hydrogen content in the material. Measurements were performed using the PBR instrument at the NIST Center for Neutron Research, and the data were analyzed using the Ref11D software package.<sup>33</sup> The 120 nm film was partially reduced at 575 °C for 120 h simultaneously with the two films examined with RSM. We fit the reflectivity data and deduced a total thickness of 124.3 nm, shown in Figure 5. The data required four layers to achieve a proper fit—a lower scattering



**Figure 5.** Neutron reflectivity data with fit (top) accompanied by the corresponding SLD profile as a function of depth (bottom). The profile demonstrates that significant changes must have occurred in the film, either structural or compositional, during reduction to account for the decreased SLD. Error bars represent  $\pm 1$  standard deviation.

length density (SLD) interfacial region and two reduced SLD regions on top of a  $\sim$ 52 nm thick bulk-like layer. The material's SLD is the volume-average of the individual atoms' coherent scattering lengths. The regions with decreased SLD in the reflectivity depth profile shall be attributed to a reduced atomic density, either through increased unit cell volume or increased porosity, or to the replacement of host atoms with species with lower coherent scattering lengths, such as hydrogen, which has a negative coherent scattering length for neutrons.<sup>34</sup> RSM measurements suggest that the lattice constant does increase during reduction, accounting for some decrease in SLD, but it is not sufficient without a combination of the other mechanisms to account for the observed profile. The foreign species which could substitute into the rBZO are Ca, from the CaH<sub>2</sub>, or Sr, La, Ta, and Al from the substrate. The coherent scattering lengths of these materials, shown in Table S2, also cannot account for the large observed decreases in SLD, which is a strong indication of a significant amount of hydrogen and/ or oxygen vacancies present in the reduced films. Natural BZO has a SLD of 4.00  $(10^{-4} \text{ nm}^{-2})$ , and in order to decrease it to around 2.7, as observed at the LSAT/rBZO interface, would require increasing the lattice constant to ~4.8 Å from 4.2 Å. Alternately, it could also be achieved by removing one and a half oxygen per unit cell without changing the lattice constant, or removing a single oxygen per unit cell and increasing the lattice constant to  $\sim$ 4.4 Å. However, in a similar work on cobaltite perovskites, even a 17% reduction in oxygen only reduced the SLD by 8%.<sup>35</sup> Hence, oxygen vacancies alone cannot explain the reduction in SLD and a combination of defects is necessary to account for this reduction. Regardless of the exact mechanism of reduction, the incorporation of oxygen vacancies as well as hydrogen in the reduced BZO is evident in the SLD depth profile. The measured electronic carrier density only requires an activated donor concentration of 1-10% per unit cell if we assume that the carriers arise from an 80 nm thick film with a lattice constant of 0.42 nm, which gives  $\sim 10^{17}$ unit cells  $cm^{-2}$ . The observed SLD reduction requires a significantly higher concentration of hydrogen in interstitial or oxygen vacancy sites. Therefore, it is very likely that the majority of the SLD-reducing defects do not contribute carriers.

To confirm the presence of hydrogen and oxygen vacancies, secondary ion mass spectrometry (SIMS) measurements were conducted on three BZO thin films grown on LSAT substrates: the same partially reduced BZO film used for the neutron reflectivity experiments, a fully reduced BZO film (120 h at 600 °C), and an unreduced control sample grown in conditions identical to those used for the rBZO film prior to reduction except done at room temperature, in order to provide a structurally comparable (amorphous) sample, with results shown in Figure S3. The fully reduced and control samples are both nominally 125 nm thick based on measured growth rates using the same growth conditions. The integrated oxygen signal (over 148 nm) of the reduced sample decreased by  $\sim$ 5% as compared to the control. The integrated hydrogen (we refer to the H<sup>-</sup> state of hydrogen as determined by SIMS) signal of the reduced sample, however, increased by  $\sim$ 75% as compared to the control sample over the same 148 nm, with some variation in the reduced sample signal driven by film roughness and beam instabilities.

The depth profile of oxygen and H<sup>-</sup> content in the partially and fully reduced samples as compared to the control demonstrates a very strong correlation with the neutron reflectivity SLD depth profile, shown in Figure 6. The significant decrease in SLD at the film/substrate interface is



**Figure 6.** SIMS data comparing the normalized oxygen and H<sup>-</sup> signals of fully and partially reduced BZO with a control sample of amorphous unreduced BZO, assuming a nominal thickness of 125 nm. The top ~80 nm of the reduced films shows a marked increase in H<sup>-</sup> content and decrease in oxygen content, in striking agreement with the neutron reflectivity SLD profile. A distinct dip in the fully reduced sample oxygen signal at the film/substrate interface also corresponds to a similar dip in interfacial SLD. Note that the SIMS data have been plotted sharing the depth axis with the SLD profile, in contrast to typical SIMS plots which place 0 depth at the sample surface.

rather anomalous and cannot be easily explained by the composition change or volume change of the lattice. We are currently investigating the origin of this effect. The largest portion of the change in oxygen and H<sup>-</sup> concentration in the reduced films can clearly be seen to occur within the top 80 nm of the film, in agreement with the reflectivity data. The largest increase in H<sup>-</sup> content occurs in the top 20 nm of the reduced films. This suggests that the larger relative concentration of H<sup>-</sup> in the surface region potentially serves as a source of carriers. If the surface region with the lowest SLD (approximately 30 nm in depth) has a higher concentration of interstitial H<sup>-</sup> in alignment with the SIMS hydrogen profile, it would easily account for the measured free carriers with an approximate contribution of around one electron per unit cell.

#### CONCLUSIONS

In conclusion, we have successfully demonstrated electron doping of the low electron affinity perovskite oxide BZO via topochemical reaction with CaH<sub>2</sub>. Epitaxial thin films of BZO lose epitaxy through the reduction process but develop room temperature conductivity more than 5 orders of magnitude greater than unreduced films. Temperature-dependent transport measurements show resistive behavior that transitions from high-temperature Arrhenius type thermally activated to Mott VRH conduction mechanisms. Neutron reflectivity and SIMS measurements provide strong evidence for the presence of oxygen vacancies and H<sup>-</sup> occupying oxygen or interstitial sites providing the carriers in reduced BZO. Stability measurements show a gradual loss of conduction as the CaH<sub>2</sub>-treated films re-oxidize with oxidation mechanisms yet unclear. Tuning the work functions of complex oxide materials is still a novel prospect and has potential use in any application which involves surface or interfacial interactions. This work is an important first step toward the realization of tunable, airstable, low electron affinity complex oxides.

## **EXPERIMENTAL PROCEDURES**

We deposited BZO thin films using PLD on DSO and LSAT single crystal substrates purchased from Crystec GmbH using a phase-pure BZO growth target densified to >95% theoretical density via spark plasma sintering. The films were grown epitaxially in layer-by-layer growth mode, with thickness and surface structural quality verified by in situ and real-time monitoring of the 35 kV RHEED pattern. We verified the epitaxial quality and thickness of the as-grown and reduced films with thin-film XRD measurements using a Bruker D8 ADVANCE diffractometer. The as-grown films were topochemically reduced by sealing them in evacuated quartz ampoules with <0.5 g CaH<sub>2</sub>, so that even if all the hydrogen were liberated the ampoule would remain intact. The ampoules were then baked in an atmosphere at temperatures between 450 and 650 °C for up to 170 h. The reduced films were immediately immersed in n-butanol on opening the ampoules and placed in an ultrasonic bath for 3 min. After sonication, the films were stored in a nitrogen glove box. The samples were wire-bonded with Al leads in standard van der Pauw geometry. Transport measurements were conducted in a Quantum Design Physical Properties Measurement System. Hall measurements were performed in fields up to  $\pm 10$  T. Transport measurements were taken using Stanford Research Systems SR830 lock-in amplifiers. Neutron reflectivity experiments were performed using the PBR and MAGIK instruments at the NIST Center for Neutron Research. Films were depth-profiled using an IONTOF IV (Münster, Germany) ToF-SIMS system equipped with a 30 keV Bi3<sup>+</sup> liquid metal ion source for analysis and a 20  $\bar{keV} \; Ar_{2700\pm 800}{}^+$  source for sputtering, both sources striking the sample surface at an angle of 45°. Depth profiling was performed in non-interlaced mode with 1 analysis scan and 10 sputtering scans per cycle, where the analysis scan with a field of view of  $(150 \times 150) \,\mu\text{m}$  was kept inside a sputter crater with dimensions of  $(400 \times 400)$  µm. The corresponding ion doses were  $1.6 \times 10^8$  ions/ cm² (0.04 pÅ) for Bi3^+ and 3.8  $\times$   $10^{14}$  ions/cm² (6.0 nÅ) for the cluster source, per cycle. Depth calibration was made using a Dektak XT stylus profilometer (Bruker Corporation, Tucson, AZ) equipped with a 2.5  $\mu$ m radius stylus tip, having a vertical resolution of 1 nm and a lateral resolution of 16 nm. A 1 mm scan was used to ensure that a large enough region outside the crater was measured to provide sufficient area for leveling.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b06370.

Thin film growth methods, topochemical reduction methods, RSM, transport fitting coefficients, SLD information, and SIMS depth profiles (PDF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: jayakanr@usc.edu.

ORCID 0

Shanyuan Niu: 0000-002-0559-3461 Alexander J. Grutter: 0000-0002-6876-7625 Jayakanth Ravichandran: 0000-0001-5030-9143

#### **Author Contributions**

The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

## Funding

This work was supported by the Air Force Office of Scientific Research under contract FA9550-16-1-0335. T.O and M.S. acknowledge the Andrew and Erna Viterbi Graduate Student Fellowship, and S.N. acknowledges the graduate energy fellowship from Link Foundation respectively.

#### Notes

The authors declare no competing financial interest.

Certain trade names and company products are identified to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best for the purpose.

# ACKNOWLEDGMENTS

The authors gratefully acknowledge beneficial conversations with Dr. Chris Van de Walle of the University of California, Santa Barbara, the assistance of Dr. Piyush Deokar, and the use of facilities in the laboratories of Dr. Brent Melot, Prof. Steve Cronin, and Prof. Andrea Hodge at the University of Southern California, as well as the facilities of Prof. Jian Luo and assistance of Sicong Jiang at the University of California, San Diego. Data presented in this article were acquired at the Core Center of Excellence in Nano Imaging at the University of Southern California.

### REFERENCES

(1) Foo, G. S.; Polo-Garzon, F.; Fung, V.; Jiang, D.-e.; Overbury, S. H.; Wu, Z. Acid-Base Reactivity of Perovskite Catalysts Probed via Conversion of 2-Propanol over Titanates and Zirconates. *ACS Catal.* **2017**, *7*, 4423–4434.

(2) Azad, A.-M.; Subramaniam, S.; Dung, T. W. On the Development of High Density Barium Metazirconate (BaZrO<sub>3</sub>) Ceramics. J. Alloys Compd. **2002**, 334, 118–130.

(3) Kreuer, K. D. Proton-Conducting Oxides. Annu. Rev. Mater. Res. 2003, 33, 333-359.

(4) Robertson, J. Band Offsets of Wide-Band-Gap Oxides and Implications for Future Electronic Devices. J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.–Process., Meas., Phenom. 2000, 18, 1785–1791.

(5) Ding, J.; Balachandran, J.; Sang, X.; Guo, W.; Veith, G. M.; Bridges, C. A.; Rouleau, C. M.; Poplawsky, J. D.; Bassiri-Gharb, N.; Ganesh, P.; et al. Influence of Nonstoichiometry on Proton Conductivity in Thin-Film Yttrium-Doped Barium Zirconate. *ACS Appl. Mater. Interfaces* **2018**, *10*, 4816–4823.

(6) Robertson, J.; Clark, S. Limits to Doping in Oxides. Phys. Rev. B: Condens. Matter Mater. Phys. 2011, 83, 075205.

(7) Zhong, Z.; Hansmann, P. Tuning the Work Function in Transition Metal Oxides and Their Heterostructures. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 235116.

(8) Łupina, G.; Dąbrowski, J.; Dudek, P.; Kozłowski, G.; Zaumseil, P.; Lippert, G.; Fursenko, O.; Bauer, J.; Baristiran, C.; Costina, I.; Müssig, H. J. Dielectric Constant and Leakage of BaZrO<sub>3</sub> Films. *Appl. Phys. Lett.* **2009**, *94*, 152903.

(9) Chen, Y.; Chen, Y.; Ding, D.; Ding, Y.; Choi, Y.; Zhang, L.; Yoo, S.; Chen, D.; deGlee, B.; Xu, H.; others. A Robust and Active Hybrid Catalyst for Facile Oxygen Reduction in Solid Oxide Fuel Cells. *Energy Environ. Sci.* **2017**, *10*, 964–971.

(10) Ding, J.; Li, L.; Li, H.; Chen, S.; Fang, S.; Feng, T.; Li, G. Optimum Preferential Oxidation Performance of  $CeO_2$ -CuO<sub>x</sub>-RGO Composites through Interfacial Regulation. *ACS Appl. Mater. Interfaces* **2018**, *10*, 7935–7945.

(11) Ohtomo, A.; Hwang, H. Y. A High-Mobility Electron Gas at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> Heterointerface. *Nature* **2004**, *427*, 423–426.

(12) Reiner, M.; Pietschnig, R.; Ostermaier, C. Tracking the Effect of Adatom Electronegativity on Systematically Modified AlGaN/GaN Schottky Interfaces. *ACS Appl. Mater. Interfaces* **2015**, *7*, 23124–23131.

(13) Kobayashi, Y.; Hernandez, O. J.; Sakaguchi, T.; Yajima, T.; Roisnel, T.; Tsujimoto, Y.; Morita, M.; Noda, Y.; Mogami, Y.; Kitada, A.; Ohkura, M.; Hosokawa, S.; Li, Z.; Hayashi, K.; Kusano, Y.; Kim, J. e.; Tsuji, N.; Fujiwara, A.; Matsushita, Y.; Yoshimura, K.; Takegoshi,

K.; Inoue, M.; Takano, M.; Kageyama, H. An Oxyhydride of BaTiO<sub>3</sub> Exhibiting Hydride Exchange and Electronic Conductivity. *Nat. Mater.* **2012**, *11*, 507–511.

(14) Ikeda, A.; Krockenberger, Y.; Irie, H.; Naito, M.; Yamamoto, H. Direct Observation of Infinite NiO<sub>2</sub> Planes in LaNiO<sub>2</sub> Films. *Appl. Phys. Express* **2016**, *9*, 061101.

(15) Takamatsu, T.; Kato, M.; Noji, T.; Koike, Y. Low-Temperature Synthesis of the Infinite-Layer Compound  $LaNiO_2$  by Soft-Chemical Techniques. *Jpn. J. Appl. Phys.* **2010**, *49*, 093101.

(16) Dixon, E.; Hadermann, J.; Hayward, M. A. Structures and Magnetism of  $La_{1-x}Sr_xMnO_{3-(0.5+x)/2}$  (0.67 $\le x \le 1$ ) Phases. Chem. Mater. **2012**, 24, 1486–1495.

(17) Kitchen, H. J.; Saratovsky, I.; Hayward, M. A. Topotactic Reduction as a Synthetic Route for the Preparation of Low-Dimensional Mn (II) Oxide Phases: The Structure and Magnetism of LaAMnO<sub>4-x</sub> (A= Sr, Ba). *Dalton Trans.* **2010**, *39*, 6098–6105.

(18) Romero, F. D.; Burr, S. J.; McGrady, J. E.; Gianolio, D.; Cibin, G.; Hayward, M. A.  $SrFe_{0.5}Ru_{0.5}O_2$ : Square-Planar  $Ru^{2+}$  in an Extended Oxide. J. Am. Chem. Soc. **2013**, 135, 1838–1844.

(19) Tassel, C.; Seinberg, L.; Hayashi, N.; Ganesanpotti, S.; Ajiro, Y.; Kobayashi, Y.; Kageyama, H.  $Sr_2FeO_3$  with Stacked Infinite Chains of FeO<sub>4</sub> Square Planes. *Inorg. Chem.* **2013**, *52*, 6096–6102.

(20) Yajima, T.; Kitada, A.; Kobayashi, Y.; Sakaguchi, T.; Bouilly, G.; Kasahara, S.; Terashima, T.; Takano, M.; Kageyama, H. Epitaxial Thin Films of  $ATiO_{3-x}H_x$  (A= Ba, Sr, Ca) with Metallic Conductivity. *J. Am. Chem. Soc.* **2012**, *134*, 8782–8785.

(21) Yamamoto, T.; Kageyama, H. Hydride Reductions of Transition Metal Oxides. *Chem. Lett.* **2013**, *42*, 946–953.

(22) Frederikse, H. P. R.; Thurber, W. R.; Hosler, W. R. Electronic Transport in Strontium Titanate. *Phys. Rev.* **1964**, *134*, A442.

(23) Ravichandran, J.; Siemons, W.; Oh, D.-W.; Kardel, J. T.; Chari, A.; Heijmerikx, H.; Scullin, M. L.; Majumdar, A.; Ramesh, R.; Cahill, D. G. High-Temperature Thermoelectric Response of Double-Doped SrTiO<sub>3</sub> Epitaxial Films. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, 82, 165126.

(24) Li, X.-F.; Hu, Z.-Y.; Huang, B. Phase Diagram and Superconductivity of Compressed Zirconium Hydrides. *Phys. Chem. Chem. Phys.* **2017**, *19*, 3538–3543.

(25) Alay-e-Abbas, S. M.; Nazir, S.; Shaukat, A. Formation Energies and Electronic Structure of Intrinsic Vacancy Defects and Oxygen Vacancy Clustering in BaZrO<sub>3</sub>. *Phys. Chem. Chem. Phys.* **2016**, *18*, 23737–23745.

(26) Eom, K.; Choi, E.; Choi, M.; Han, S.; Zhou, H.; Lee, J. Oxygen Vacancy Linear Clustering in a Perovskite Oxide. *J. Phys. Chem. Lett.* **2017**, *8*, 3500–3505.

(27) Tufte, O. N.; Chapman, P. W. Electron Mobility in Semiconducting Strontium Titanate. *Phys. Rev.* **196**7, *155*, 796.

(28) Rowberg, A. J. E.; Weston, L.; Van de Walle, C. G. Optimizing Proton Conductivity in Zirconates Through Defect Engineering. *ACS Appl. Energy Mater.* **2019**, *2*, 2611–2619.

(29) Vining, C. B. A Model for the High-Temperature Transport Properties of Heavily Doped n-Type Silicon-Germanium Alloys. J. Appl. Phys. **1991**, 69, 331–341.

(30) Knotek, M. L.; Pollak, M. Correlation Effects in Hopping Conduction: Hopping as a Multi-Electron Transition. J. Non-Cryst. Solids 1972, 8–10, 505–510.

(31) Efros, A. L.; Shklovskii, B. I. Coulomb Gap and Low Temperature Conductivity of Disordered Systems. J. Phys. C: Solid State Phys. 1975, 8, L49–L51.

(32) van Hapert, J. J. Hopping Conduction and Chemical Structure: A Study on Silicon Suboxides. Ph.D. Dissertation, Utrecht University, Utrecht, Netherlands, 2002.

(33) Kirby, B. J.; Kienzle, P. A.; Maranville, B. B.; Berk, N. F.; Krycka, J.; Heinrich, F.; Majkrzak, C. F. Phase-Sensitive Specular Neutron Reflectometry for Imaging the Nanometer Scale Composition Depth Profile of Thin-Film Materials. *Curr. Opin. Colloid Interface Sci.* **2012**, *17*, 44–53.

(34) Rehm, C.; Fritzsche, H.; Maletta, H.; Klose, F. Hydrogen Concentration and its Relation to Interplanar Spacing and Layer Thickness of 1000-Å Nb (110) Films During in situ Hydrogen Charging Experiments. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 3142.

(35) Gilbert, D. A.; Grutter, A. J.; Murray, P. D.; Chopdekar, R. V.; Kane, A. M.; Ionin, A. L.; Lee, M. S.; Spurgeon, S. R.; Kirby, B. J.; Maranville, B. B.; Mehta, A. Ionic Tuning of Cobaltites at the Nanoscale. *Phys. Rev. Mater.* **2018**, *2*, 104402.