
01 Jan 2005

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Recommended Citation

S. K. Patil et al., "Fourier Transform Infrared Analysis of Hydroxyl Content of Hydrothermally Processed Heteroepitaxial Barium Titanate Films," *Journal of Material Research*, Material Research Society, Jan 2005.

The definitive version is available at <https://doi.org/10.1557/JMR.2005.0406>

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Fourier transform infrared analysis of hydroxyl content of hydrothermally processed heteroepitaxial barium titanate films

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(Received 15 November 2004; accepted 26 July 2005)

The concentration of hydroxyl ($-OH$) groups in epitaxial barium titanate ($BaTiO_3$) films (thickness ~ 200 nm), deposited on single-crystal strontium titanate ($SrTiO_3$) at 150 °C by a hydrothermal technique, was investigated using x-ray photoelectron spectroscopy and Fourier transform infrared (FTIR) spectroscopy. After hydrothermal treatment, a broad FTIR resonance for the hydroxyl groups indicated a significant concentration of surface $-OH$ groups in the films. The as-deposited films were subsequently treated hydrothermally with D_2O , and the kinetics of the exchange reaction between $-OH$ incorporated into the film and $-OD$ from the D_2O were studied using FTIR. For reactions carried out intermittently, the kinetics of the exchange reaction between $-OH$ by $-OD$ depended not only on the total reaction time, but also on the duration of each treatment. The broad FTIR hydroxyl resonance in the as-deposited hydrothermal film was significantly reduced only after heating for 1 h at 600 – 800 °C.

I. INTRODUCTION

Barium titanate ($BaTiO_3$) thin films are of significant interest for several applications in the electronics industry because of their high-dielectric constant and ferroelectric properties.¹ Conventional routes to the synthesis of $BaTiO_3$ films, such as sol-gel processing and vapor phase methods (e.g., metalorganic chemical vapor deposition, sputtering, and pulsed laser deposition), often require high temperatures or high vacuum. There is interest in solution-based methods, such as hydrothermal and electrochemical techniques, because these techniques can provide direct routes to the synthesis of crystalline $BaTiO_3$ films at low temperatures.^{2–19} The hydrothermal route employs reactions in aqueous solutions at temperatures close to, or above, the boiling point of water to

deposit crystalline inorganic materials in the form of particles, thin films, or crystals.²⁰

Hydrothermal deposition of heteroepitaxial $BaTiO_3$ films on structurally similar single-crystal substrates, such as $SrTiO_3$ and $LaAlO_3$, has been demonstrated.^{6,10,13,19} Structural investigations of crystalline $BaTiO_3$ powders, precipitated under hydrothermal conditions similar to those used for the preparation of heteroepitaxial $BaTiO_3$ films, indicate that defects and impurities such as Ba and Ti vacancies, H_2O , $-OH$, and carbonate ions may be incorporated into the crystal lattice during synthesis.^{21–24} The concentration of these incorporated species depends on synthesis conditions such as temperature, pH, Ba concentration, and time. Electrical characterization of epitaxial $BaTiO_3$ films, deposited hydrothermally on single-crystal $SrTiO_3$ substrates at 90 °C, indicates that the incorporated H_2O and $-OH$ lead to undesirably high dielectric losses.^{25,26} The concentration of $-OH$ and H_2O can be significantly reduced only after heat treatment at temperatures in the range of

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DOI: 10.1557/JMR.2005.0406

600–800 °C.^{22–25} The relationships between the heat treatment of powders and films and their electrical properties have also been examined.^{25,26}

Several studies have been performed to understand the incorporation of H₂O and –OH in hydrothermal BaTiO₃ powders and films^{22–25,27–30} because these species lead to deterioration of dielectric properties. However, a clear understanding of the nature of the incorporation and mechanism of removal of these species is still lacking. Some information on the presence and location of –OH groups has been obtained using a variety of techniques, including x-ray photoelectron spectroscopy (XPS) and infrared analysis (IR). These techniques have been used in this work to further elucidate the nature of hydroxyl groups in hydrothermally synthesized BaTiO₃.

XPS is a method of surface analysis in which a sample is irradiated, in high vacuum, with x-rays, which cause photoemission of electrons, typically from a surface layer of ~2 nm.^{31–33} Photoelectrons emitted from atomic core levels are detected as a function of energy. Shifts in the core-level energies give information on the chemical environment of the atoms. Although truly surface sensitive, the technique can be used to determine the composition of deeper layers, normally achieved by sequential (or simultaneous) removal of surface layers by ion beam sputtering and XPS analysis. XPS analysis of films and powders of BaTiO₃, as well as the isostructural SrTiO₃, commonly shows an asymmetrical peak in the O 1s spectrum, which can often be fitted with two Gaussian peaks.^{28,34–38} The main O 1s peak, at a lower binding energy (in the range of ~529.5–530 eV) is ascribed to O in the titanate lattice.³⁴ The second oxygen peak (~1.5–2.0 eV higher than the titanate oxygen peak) is ascribed to hydroxyl species.³⁴ The intensity of this hydroxyl peak is commonly found to be surface sensitive, in that the intensity decreases with depth.

In Fourier transform infrared (FTIR), the vibrational modes of molecules in a sample are studied by monitoring the absorption or emission of IR radiation in ambient conditions.^{39,40} After deconvolution and Fourier analysis of the data, the FTIR spectrum provides chemical information about the bonding structure of molecules on the surfaces as well as in the bulk of the sample. FTIR analysis of BaTiO₃ powders and thin films prepared by hydrothermal techniques commonly show a broad resonance for the –OH stretching vibration in the range of 3000–3600 cm⁻¹.^{23–25,29} This broad band is ascribed to surface-adsorbed –OH groups because of their adsorption on many surface sites.^{23,29} Its intensity is significantly reduced only after heating to temperatures of 600–800 °C.^{23–25} In addition to the broad resonance, a few studies on hydrothermal BaTiO₃ particles have also observed a sharp adsorption band in the range of 3462.5–3505.5 cm⁻¹. This sharp band has been ascribed to H₂O or –OH defects in the BaTiO₃ lattice.^{23,29,41}

Deuteration of hydrothermal BaTiO₃, in which –OH groups are exchanged for –OD groups, has been used to distinguish better the location of the –OH groups. By treating hydrothermal BaTiO₃ powders in D₂O for 16 h at 150 °C, Hennings et al.²² found that a large number of the –OH groups was replaced by –OD in the IR spectra. The –OD absorption decreased significantly after annealing the sample at 400 °C, but the –OH absorption remained strong even at this temperature. Chien et al.²⁵ used deuterium nuclear magnetic resonance (NMR) to verify the presence of –OD within the lattice of BaTiO₃ powders synthesized in the presence of D₂O. They found two components in the spectrum: a narrow component due to D₂O trapped between the crystallites and a broad component due to D₂O or –OH trapped within the BaTiO₃ lattice. NMR also revealed the presence of H₂O or –OH in the lattice of hydrothermal PbTiO₃ powders and films.⁴²

In the present work, the nature and concentration of H₂O and –OH groups incorporated into hydrothermal BaTiO₃ films were examined using XPS and FTIR spectroscopy. Hydrothermal treatment of the as-deposited films in D₂O was used to understand the mechanism of the H₂O and –OH incorporation. An important part of the work was the measurement, using FTIR, of the kinetics of the exchange reaction between –OH incorporated into the film and –OD from the D₂O. Since the exchange reaction for surface –OH groups is expected to be faster than that for lattice –OH, measurement of the reaction kinetics may provide additional insight into –OH incorporation in hydrothermal BaTiO₃.

II. EXPERIMENTAL PROCEDURE

The starting materials and experimental procedure for the hydrothermal deposition of BaTiO₃ films on single-crystal SrTiO₃ substrates are described in detail in earlier work.¹⁹ Briefly, 4 g Ba(OH)₂·8H₂O were added to 24 cm³ de-ionized water (previously boiled for 1 h to remove CO₂) in a Teflon-lined autoclave (45 ml; Parr Instrument Co., Moline, IL) to give a 0.5 M Ba(OH)₂ solution. The system was purged with argon, sealed and heated for 3 h at 90 °C to dissolve the Ba(OH)₂. One gram of TiO₂ powder was added to the solution (pH = 13.3) and a single crystal of {100} SrTiO₃ (polished on both sides) was suspended in the solution using Teflon thread. The autoclave was sealed and the system was heated to 150 °C in 10 min. After 12 h reaction, the coated SrTiO₃ substrate was washed twice for 15 min with de-ionized water in an ultrasonic bath, dried for at least 12 h at ~80 °C, and stored in a vacuum desiccator.

The exchange reaction between the –OH groups incorporated into the as-deposited, hydrothermal film and –OD from a D₂O medium was carried out by submerging the coated substrate in 10 cm³ D₂O in a Teflon-lined

autoclave. After closing the autoclave, the system was heated to 150 °C in 10 min and held at this temperature for the required time. The coated substrate was removed from the vessel, dried at 60 °C in a vacuum oven, and stored in a vacuum desiccator. The exchange reaction was carried out intermittently, with the duration of each treatment varying for each sample. One sample was subjected to several individual exchange reactions lasting 1 h each. After each 1-h treatment, the sample was removed from the vessel, dried, and analyzed using FTIR as described below. A second sample was treated similarly but with individual exchange reactions lasting for two hours. A third sample was reacted for intervals of 5 h.

The microstructure of the as-deposited films was observed using field emission scanning electron microscopy (FESEM; Hitachi S4700). XPS (AXIS 165; KRATOS, Kyoto, Japan) was used to detect the presence of H₂O and –OH in the as-deposited films. XPS scans were performed in the O 1s region of the spectrum (525–535 eV), using the C 1s peak at 284.6 eV as an internal standard. Sputtering was performed for 30 min with Ar ions to probe the regions inside the BaTiO₃ film. Deconvolution of the spectra into separate peaks was performed using a curve-fitting routine that assumed a Gaussian line shape and an S-shaped background.

FTIR spectroscopy in the mid-IR range was performed on the as-deposited films and the deuterated films using a Nicolet Magna-IR 750 Spectrometer (Thermo Electron Corp., Madison, WI). Prior to the analysis, the samples were kept in a vacuum desiccator. The FTIR scans were taken in absorbance mode. In the analysis, the empty sample chamber was first purged for 1 h and a background FTIR spectrum was taken. After inserting the sample, the chamber was again purged for 1 h, after which the FTIR spectrum of the sample was taken. For each run, 512 scans were made, with the resolution at 4 or 8 cm⁻¹, depending on the background noise. Standard software (FTIR Spectrum V.200, Thermo Electron Corp., Madison, WI) was used to determine the areas under the –OH and –OD bands in the spectra.

The as-deposited hydrothermal films were also heated for 1 h at temperatures in the range of 200–800 °C. The heating and cooling rates were 10 °C/min. A different film was used for each heat treatment. Heating was performed in static air, in a programmable furnace (Model DT-31-FL; Deltech, Denver, CO). After the heat treatment, the films were stored in a vacuum desiccator prior to analysis by FTIR using the same procedure outlined earlier.

III. RESULTS AND DISCUSSION

A. Characteristics of the deposited BaTiO₃ film

A FESEM micrograph of the surface of a BaTiO₃ film on a single-crystal SrTiO₃ substrate is shown in Fig. 1.

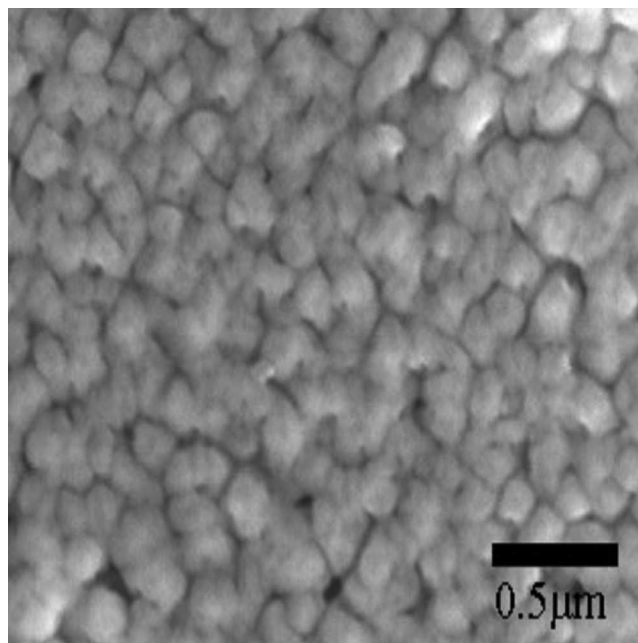


FIG. 1. SEM micrograph of BaTiO₃ thin film grown on single-crystal SrTiO₃ substrate, showing nearly complete coverage of the substrate.

This micrograph is representative of the films used in the experiments. The substrate was almost completely covered by the BaTiO₃ film, but a few pores and pinholes are visible. The individual crystals, with a linear dimension of ~200 nm, are separated by boundaries. Previous work showed that the films were epitaxial.¹⁹

XPS spectra are shown in Fig. 2 for the O 1s peak from the surface of the as-deposited BaTiO₃ film and from a point within the film produced after 30 min of Ar sputtering. A good fit of the results was obtained by using two peaks. The main peak at the lower binding energy of 529.3 eV is attributed to O from the BaTiO₃ structure.^{34,38} The second oxygen peak seen at a higher binding energy of 531.1 eV, approximately 1.8 eV higher than the titanate oxygen peak, is attributed to O from –OH species.^{34,38} No clear evidence was found for the presence of barium carbonate species, which, if present, should produce an O 1s peak 3 eV higher than the titanate O 1s peak.³⁴

After sputtering, the intensity of the hydroxyl O 1s peak decreased significantly relative to the titanate O 1s peak but did not disappear. The films used in the experiments contained only a few pores and pinholes, so the possible locations for hydroxyl species in the sputtered films are mainly the BaTiO₃ lattice and the crystal (or grain) boundaries perpendicular to the plane of the film. As outlined earlier, the presence of H₂O or –OH species in the BaTiO₃ lattice of powders and films has been detected by techniques such as IR and NMR.^{23,25} In the present work, the sputtering area (on the order of square

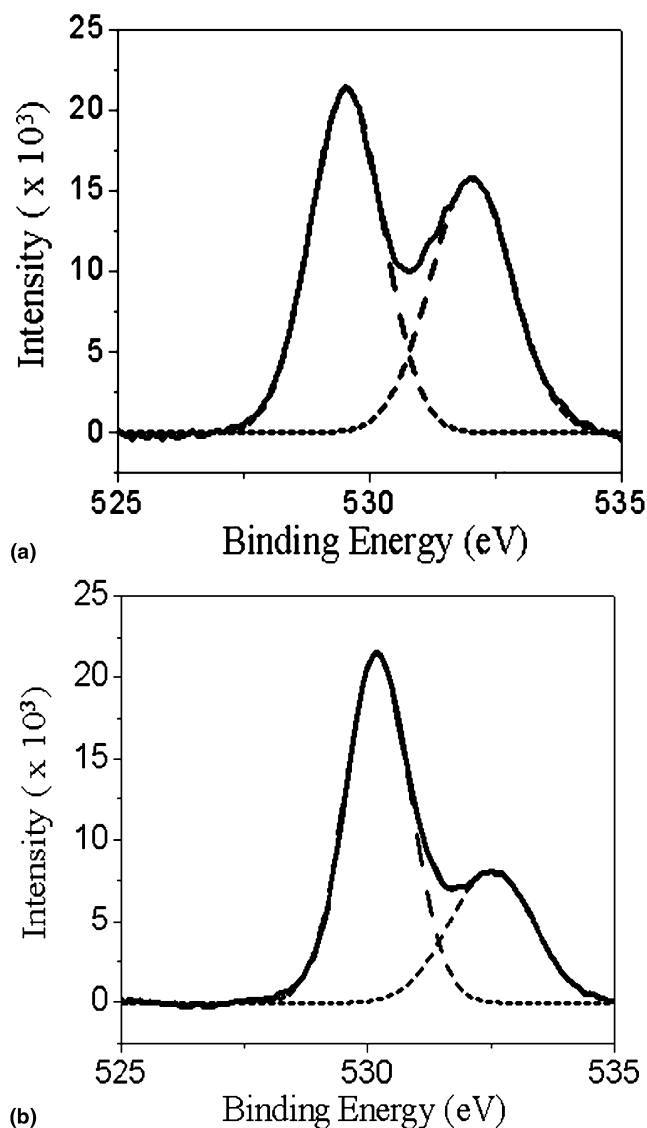


FIG. 2. XPS spectra for the O 1s peak (a) from the surface of the as-deposited BaTiO₃ film and (b) from within the film produced after 30 min of Ar ion sputtering.

millimeters) and, hence, the XPS analysis area, is significantly larger than the size of the crystals (linear dimension ~ 200 nm) in the film (see Fig. 1), so the analysis area includes the grain boundaries. However, systematic studies by Waser,⁴³ using thermal desorption and electrical conductivity measurements to determine the possible locations of hydrogen defects in BaTiO₃ materials, indicate that the grain boundaries do not act as the dominant location for hydrogen incorporation. Hydroxyl groups in the lattice are therefore expected to provide the main contribution to the observed hydroxyl O 1s peak for the sputtered films.

The FTIR spectra of the SrTiO₃ single-crystal substrate (without a BaTiO₃ film) and of the BaTiO₃ film deposited on the SrTiO₃ substrate are shown in Fig. 3.

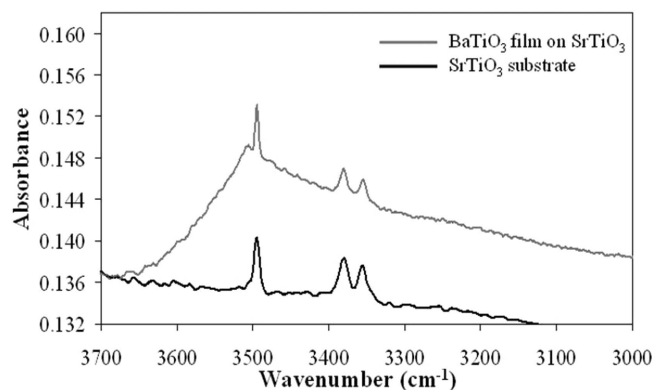


FIG. 3. FTIR spectra of the uncoated SrTiO₃ single crystal substrate and the substrate after hydrothermal deposition of a BaTiO₃ film. The peak at ~ 3496 cm⁻¹ is ascribed to the -OH stretching vibration.

For the spectrum of the uncoated substrate, a sharp peak was observed at ~ 3496 cm⁻¹, along with two smaller peaks at ~ 3381 and ~ 3358 cm⁻¹. The peak at ~ 3496 cm⁻¹ is ascribed to the -OH stretching vibration.^{22,23,25,41} It is attributed to H₂O or -OH incorporated into the single-crystal substrate as a result of the water-based polishing process used by the manufacturer. The two smaller peaks have not been assigned. There have been no sharp resonances in this region assigned to SrTiO₃.

The spectrum for the BaTiO₃ film deposited on SrTiO₃ substrate (Fig. 3) shows a broad band in the wave number range of 3000–3600 cm⁻¹. It has been reported that -OH groups adsorbed on the surface of the BaTiO₃ film exhibit a broad resonance in this range because of the availability of many different surface adsorption sites.^{23,29} In the spectrum of the coated substrate, a sharp absorbance peak is also observed at the same wavenumber (~ 3496 cm⁻¹) as that for the uncoated substrate. It cannot be clearly determined whether the sharp peak can be attributed to -OH groups in both the SrTiO₃ substrate and the BaTiO₃ film or in the SrTiO₃ substrate alone. However, in the case of hydrothermal BaTiO₃ powders, a relatively sharp peak occurring at a similar wave number (~ 3496 cm⁻¹) was observed by Noma et al.²³ and attributed to the absorbance of -OH groups incorporated into the BaTiO₃ lattice. Since hydrothermal BaTiO₃ films are commonly synthesized under conditions similar to those for powders, it is therefore likely that the sharp peak at ~ 3496 cm⁻¹ may be associated with -OH groups in both the BaTiO₃ film and the SrTiO₃ substrate.

B. Kinetics of exchange reaction between -OH in the BaTiO₃ film and -OD from D₂O

The FTIR spectra of the substrate coated with a BaTiO₃ film are shown in Fig. 4 after (i) three individual treatments of 1 h each in D₂O, (ii) five individual treatments lasting 1 h each in D₂O, and (iii) one treatment lasting 5 h. For comparison, the spectrum of the coated

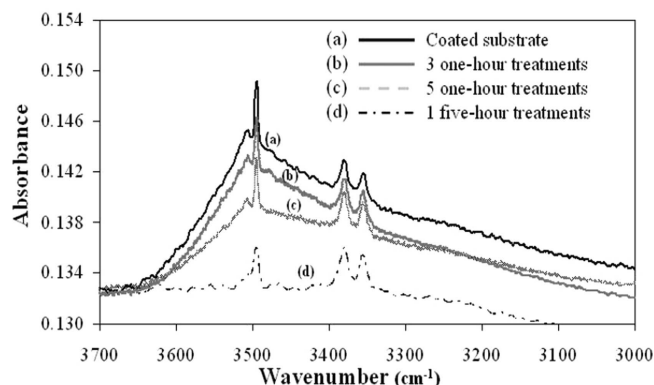


FIG. 4. FTIR spectra showing the -OH band for the BaTiO_3 -coated substrate prior to D_2O treatment, and after three 1-h treatments, five 1-h treatments, and one 5-h treatment in D_2O .

substrate without any treatment in D_2O is also shown. The intensity of the broad -OH band ($3000\text{--}3600\text{ cm}^{-1}$), taken as the area under the curve after subtracting the spectrum of the substrate, is found to decrease with increasing treatment time in D_2O , indicating replacement of the -OH in the film by -OD . Concurrent with the decrease in the -OH intensity, a distinct band in the $2450\text{--}2650\text{ cm}^{-1}$ range, attributable to the -OD groups that have replaced the -OH groups in the film, develops in the spectra (Fig. 5). The intensity of the -OD band increases with the D_2O treatment time.

The data in Figs. 4 and 5 suggest that, for a given total reaction time, the kinetics of the exchange reaction between -OH and -OD depend on the duration of the individual intermittent treatments. For example, the intensity of the -OH band for the sample treated in five individual runs lasting 1 h each is significantly higher than that for the sample treated in one run lasting 5 h. To further investigate the influence of the duration of the individual runs on the exchange kinetics, coated substrates were treated in D_2O for different time intervals, and the FTIR spectra were measured after each run. Figures 6 and 7 show the spectra for the -OH and -OD

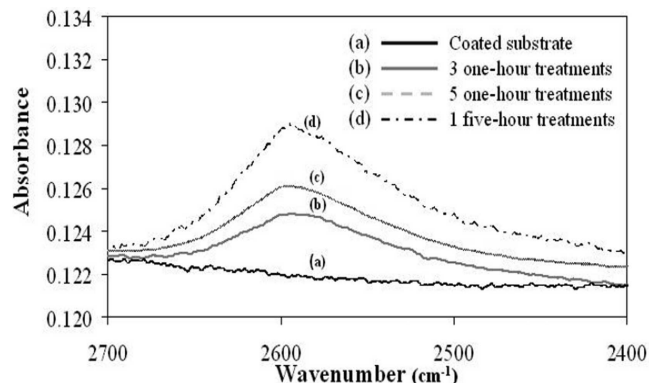


FIG. 5. FTIR spectra of the -OD band for the BaTiO_3 -coated substrate subjected to the D_2O treatment described in Fig. 4.

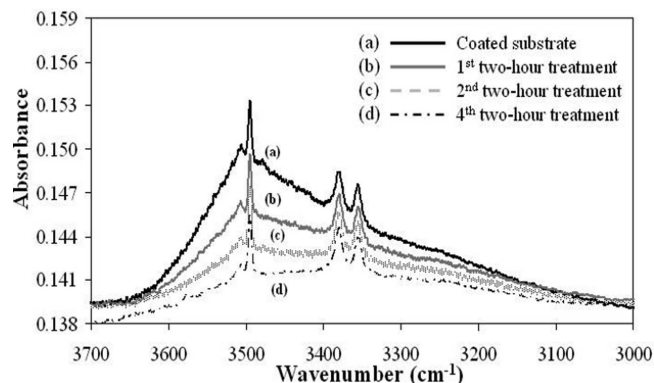


FIG. 6. FTIR spectra of the -OH band for the BaTiO_3 -coated substrate after individual treatments in D_2O lasting 2 h each.

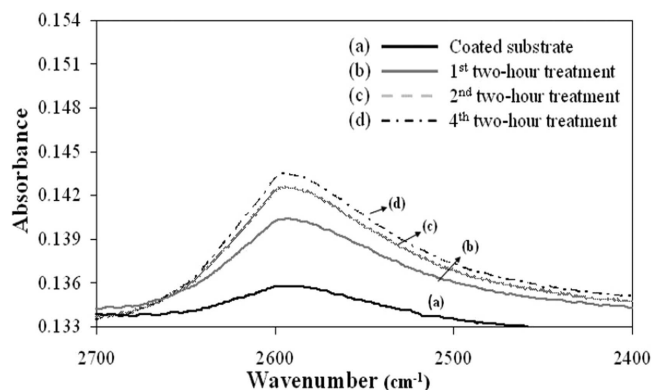


FIG. 7. FTIR spectra of the -OD band for BaTiO_3 -coated substrate subjected to the D_2O treatment described in Fig. 6.

bands for samples treated in D_2O when the duration of the individual runs was 2 h. These two sets of spectra are consistent with a first-order decay of the -OH intensities and increases of the -OD intensities.

The resonance intensities for the -OH and -OD bands as functions of the cumulative treatment time for a coated substrate treated for 2 h intervals in D_2O are shown in Figs. 8(a) and 8(b). Both curves show exponential decay/buildup. The data for the substrates treated for 1 h intervals show similar trends and are omitted to maintain conciseness. The change in the -OH or the -OD band intensity (area) can be described by an equation of the form

$$\Delta y = \Delta y_{\max}(1 - e^{-t/\tau}) \quad (1)$$

where $\Delta y = y_o - y$, and $\Delta y_{\max} = y_o - y_f$, y is the area at time t , y_o is the initial area, y_f is the final (limiting) area, and τ is the time constant for the exchange reaction. Equation (1) can also be written as

$$y = A + Be^{-t/\tau} \quad (2)$$

where $A = y_f$ and $B = (y_o - y_f)$. Table I gives the values for A , B , and τ obtained from a least squares fit to the data for the 1 and 2 h duration treatments. The time

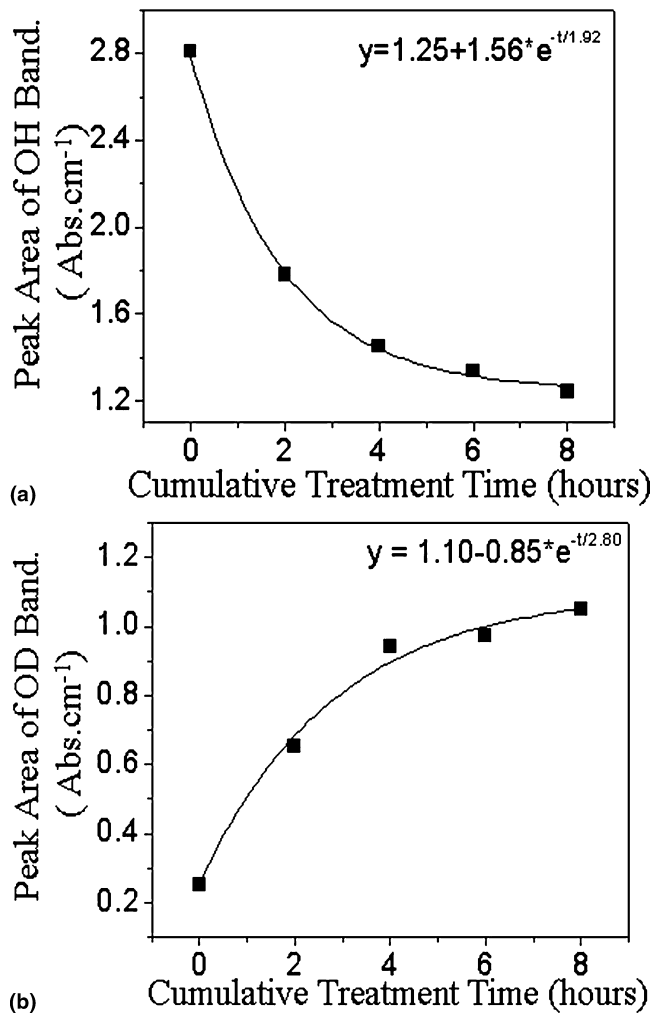


FIG. 8. Areas of (a) the $-\text{OH}$ band and (b) the $-\text{OD}$ band versus the total time of D_2O treatment, for coated substrates subjected to 2-h individual treatments.

TABLE I. Kinetic parameters for the exchange reaction between $-\text{OH}$ and $-\text{OD}$.

Treatment interval	Species	A (Abs cm^{-1})	B (Abs cm^{-1})	τ (h)
1 h	$-\text{OH}$	2.82	0.46	0.94
	$-\text{OD}$	0.25	-0.26	1.34
2 h	$-\text{OH}$	1.25	1.56	1.92
	$-\text{OD}$	1.10	-0.85	2.80

constants for the exchange reaction for the 2 h duration are ~ 2 times the values for the 1 h treatments. The time constants for the $-\text{OD}$ intensity build-up are ~ 1.5 times the decay time constant for the $-\text{OH}$ band intensity. In an exchange reaction where each $-\text{OH}$ was replaced directly by an $-\text{OD}$, the time constants for $-\text{OH}$ decay and $-\text{OD}$ buildup are expected to be equal. The observed difference in time constants indicates that the buildup of $-\text{OD}$ occurs more slowly than the decay of $-\text{OH}$. Whereas the

significance of the kinetic parameters for the exchange reaction is unclear at present, the data indicate that the rates at which $-\text{OH}$ species in the BaTiO_3 film are replaced by $-\text{OD}$ are rather slow. Furthermore, for a given cumulative reaction time, the concentration of $-\text{OH}$ replaced by $-\text{OD}$ is smaller for the 1 h duration reaction than for the 2 h duration reaction.

C. FTIR analysis of thermally treated BaTiO_3 films

FTIR spectra, in the $-\text{OH}$ stretching region, of hydrothermal BaTiO_3 films heated for 1 h at 400, 600, and 800 $^\circ\text{C}$ are shown in Fig. 9. For comparison, the FTIR spectrum of the as-deposited BaTiO_3 films is also shown. The broad spectrum attributable to $-\text{OH}$ groups decreases with increasing treatment temperature. The broad $-\text{OH}$ resonance was almost eliminated only after heating for 1 h at 600–800 $^\circ\text{C}$, as observed in previous studies.^{23–25} The spectrum of the film heated at 800 $^\circ\text{C}$ has three sharp peaks (a larger peak at 3496 cm^{-1} along with two smaller peaks at 3381 and 3358 cm^{-1}) that correspond to the peak positions observed for the uncoated SrTiO_3 substrate (see Fig. 3).

D. Kinetics and mechanism of $-\text{OH}$ removal in hydrothermal BaTiO_3 films

The XPS data indicated the presence of $-\text{OH}$ species, not only at the surface of the film, but also incorporated within the BaTiO_3 lattice (Fig. 2). A sharply defined peak was present in the $-\text{OH}$ band of the FTIR spectra (Fig. 3) which corresponded to lattice $-\text{OH}$ species in the SrTiO_3 substrate and presumably in the BaTiO_3 film. The relative contributions of the film and the substrate to the sharp FTIR peak cannot be clearly distinguished in the present work. However, IR analysis of hydrothermal BaTiO_3 powders by Noma et al.²³ indicated a well-defined peak at approximately the same wave number. The intensity of this peak was considerably smaller than that of the broad band in the wave number range of

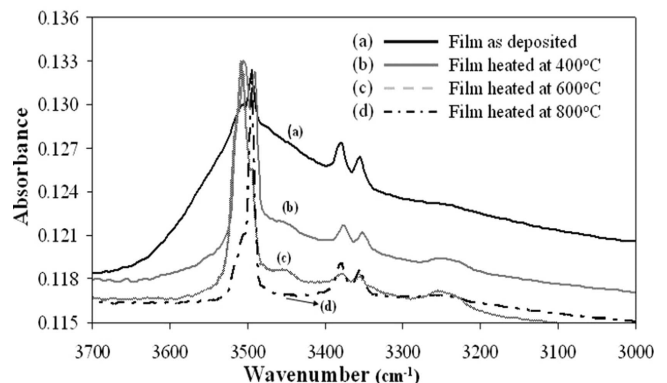


FIG. 9. FTIR spectra of BaTiO_3 films on SrTiO_3 substrate after heat treatment for 1 h at 400–800 $^\circ\text{C}$.

3000–3600 cm^{-1} , attributed to surface –OH species, so therefore it had little effect on the measured exchange reaction kinetics for as-deposited BaTiO_3 films treated in D_2O .

The exchange reaction kinetics between –OH incorporated into the films and –OD from the D_2O medium depended not only on the total time of the reaction but also on the duration of each individual treatment. The ability to undergo exchange was reduced for smaller duration treatments. This may indicate that a reaction barrier must be overcome at the start of each treatment, an intermediate reaction occurs, or that the –OD partially desorbs after each treatment. Current work is aimed at achieving a clearer understanding of the nature of –OH incorporation in hydrothermal BaTiO_3 films and at developing a model for the exchange reaction between –OH in the film and –OD from D_2O .

IV. CONCLUSIONS

FTIR investigations of as-deposited, hydrothermal BaTiO_3 films on single-crystal SrTiO_3 substrates revealed a spectrum with a broad –OH band in the wave number range of 3000–3600 cm^{-1} , indicating the presence of a significant concentration of surface –OH groups in the film. A sharply-defined peak at $\sim 3496 \text{ cm}^{-1}$, attributed to lattice –OH species, was also found but the contribution from the BaTiO_3 film cannot be clearly distinguished from that of the SrTiO_3 substrate. When treated in D_2O , the kinetics of the exchange reaction between –OH incorporated into the films and –OD from D_2O followed first-order kinetics and depended on the total reaction time as well as on the time interval of individual treatments in intermittent reactions. As the total reaction time increased, the concentration of –OH groups replaced by –OD increased, but for a given reaction time, the amount of –OH exchanged was smaller for shorter duration reactions and larger for longer duration runs. The time constant for the exchange reaction was smaller for shorter duration reactions. The broad FTIR spectrum in the as-deposited BaTiO_3 film disappeared only after heat treatment for 1 h at 600–800 $^\circ\text{C}$, indicating that the surface –OH groups are strongly chemisorbed.

ACKNOWLEDGMENTS

This work was supported by the American Chemical Society, The Petroleum Research Fund, ACS-PRF# 37026-AC5. FDB acknowledges the support of the National Science Foundation under Grant No. DMR-0412320. The authors would like to thank the anonymous reviewer whose insightful comments have helped to strengthen the manuscript.

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