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Disciplines
Engineering | Materials Science and Engineering

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The formation and electronic structure of bulk and surface oxygen vacancies in BaTiO$_3$ have been studied previously. In general, it has been found that single crystal BaTiO$_3$ can be chemically reduced by annealing in vacuum $T=900$–1200 K, as indicated by a progressive change in the sample color from light yellow to green, and eventually to blue and black. In the present work, temperature programmed desorption (TPD) is used to further examine some of these interactions, as well as how they are affected by changes in the crystal surface stoichiometry. The TPD results indicate that oxygen vacancies are the active sites for the room temperature adsorption of methanol and carbon dioxide on BaTiO$_3$(001).

The surface behavior of ferroelectric materials is currently of significant interest due in part to proposals for new approaches to catalysis, sensing, and nanodevices. These applications are all based on the same underlying principle: oppositely poled surfaces of a ferroelectric material exhibit different chemical and physical properties. Asymmetric surface properties have been observed, for example, in experiments involving chemical etching, thermally induced and photoinduced electron emission, measurements of polarization-dependent surface conductivity, and solution-based deposition of particles onto ferroelectric substrates. Recently, it has also been found that the adsorption and desorption energetics of various molecules (e.g., alcohols, acetic acid, carbon dioxide, and water) on ferroelectric substrates [e.g., LiNbO$_3$, BaTiO$_3$, and Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ or PZT] are affected by the substrate polarization.

Predicting the effect of polarization reversal on molecule-surface interactions is challenging because there are several factors to consider, including electrostatic effects due to surface polarization charge and screening charge as well as possible differences in the stoichiometry and arrangement of atoms at oppositely poled surfaces. However, molecular adsorption on surfaces is often site specific, so one way to address this challenge is to identify the adsorption sites for molecules on a given surface and then to examine how polarization reversal affects the electronic and geometric structure of these sites, for example, through the use of scanning probe microscopy techniques. This article is concerned with the first part of this strategy, identifying the nature of molecular adsorption sites on a ferroelectric material, which in this case is barium titanate (BaTiO$_3$). Recent adsorption studies on barium titanate surfaces have indicated that several molecules (carbon dioxide, methanol, ethanol, and 2-fluoroethanol) adsorb at oxygen vacancy sites at room temperature through a precursor-mediated mechanism. In the present work, temperature programmed desorption (TPD) is used to further examine some of these interactions, as well as how they are affected by changes in the crystal surface stoichiometry. The TPD results indicate that oxygen vacancies are the active sites for the room temperature adsorption of methanol and carbon dioxide on BaTiO$_3$(001).

I. INTRODUCTION

Ferroelectric materials naturally exhibit a spontaneous polarization that can be reversed under the influence of an applied electric field. The surface behavior of ferroelectric materials is currently of significant interest due in part to proposals for new approaches to catalysis, sensing, and nanodevices. These applications are all based on the same underlying principle: oppositely poled surfaces of a ferroelectric material exhibit different chemical and physical properties. Asymmetric surface properties have been observed, for example, in experiments involving chemical etching, thermally induced and photoinduced electron emission, measurements of polarization-dependent surface conductivity, and solution-based deposition of particles onto ferroelectric substrates. Recently, it has also been found that the adsorption and desorption energetics of various molecules (e.g., alcohols, acetic acid, carbon dioxide, and water) on ferroelectric substrates [e.g., LiNbO$_3$, BaTiO$_3$, and Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ or PZT] are affected by the substrate polarization.

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The formation and electronic structure of bulk and surface oxygen vacancies in BaTiO$_3$ have been studied previously. In general, it has been found that single crystal BaTiO$_3$ can be chemically reduced by annealing in vacuum $T=900$–1200 K, as indicated by a progressive change in the sample color from light yellow to green, and eventually to blue and black. In the present work, temperature programmed desorption (TPD) is used to further examine some of these interactions, as well as how they are affected by changes in the crystal surface stoichiometry. The TPD results indicate that oxygen vacancies are the active sites for the room temperature adsorption of methanol and carbon dioxide on BaTiO$_3$(001).

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cancies can be generated by Ar-ion bombardment. These defects can be detected by surface sensitive techniques such as photoemission spectroscopy. For example, Courths used photoemission, low energy electron diffraction (LEED), and Auger electron spectroscopy (AES) to study the BaTiO$_3$(001) surface under various conditions. A stable 1 × 1 structure with a low intensity state in the band gap could be produced by Ar- or O-ion sputtering followed by annealing in ultrahigh vacuum (UHV) to 1100 K. The intensity of the band gap emission state is sensitive to sample annealing conditions: it is greatest when the surface is freshly sputtered or after prolonged vacuum annealing, and it is suppressed upon annealing in 5 × 10$^{-5}$ torr O$_2$ or exposure to O$_2$ at room temperature. Based on these observations, the band gap state is attributed to Ti$^{3+}$–O vacancy complexes on the surface. These defects have also been imaged by scanning tunneling microscopy and spectroscopy (STM/S) on UHV-annealed BaTiO$_3$(100).

The relatively small number of BaTiO$_3$ surface studies have also provided insight into the arrangement of atoms at single crystal surfaces. The perovskite crystal structure of BaTiO$_3$ has two possible bulk [001] surface terminations. STM images of BaTiO$_3$(100) and (001) annealed in vacuum at high temperatures ($T=1270$–1570 K) have revealed flat terraces with step edges of unit cell height. These observations suggest that one of the two bulk terminations (BaO or TiO$_2$) is stable at high temperatures. There is some evidence in these studies that the TiO$_2$ termination is favored, but it is not entirely clear. Calculations indicate that the thermodynamic stabilities of the two surfaces are comparable. Other studies have provided evidence for surface reconstructions and the decomposition of BaTiO$_3$ at the crystal surface. For example, core-level photoemission spectroscopy suggests that several Ba–O phases exist in the (100) surface layer after annealing in UHV. Ba surface enrichment has also been observed by AES and ion scattering spectroscopy on surfaces annealed to high temperatures with oxygen. In addition, high resolution electron microscopy shows the presence of separate Ti–O and Ba–O phases on the surface, as a result of BaTiO$_3$ decomposition under electron irradiation. Most recently, first principles calculations combined with LEED, atomic force microscopy, and STM have identified the conditions under which Ti–O based reconstructions are stable and those that result in surface decomposition into Ba–O and Ti–O phases. It is clear from these observations that the surface structure of BaTiO$_3$ is highly sensitive to processing conditions.

II. EXPERIMENTAL PROCEDURES

A single crystal BaTiO$_3$ sample with (001) orientation was purchased from MTI Corporation. The sample was 5 × 5 × 1 mm, polished on one side and designated as substrate grade by the manufacturer. TPD measurements were performed in a UHV chamber operating at a base pressure of approximately 2 × 10$^{-10}$ torr or lower. The chamber is equipped with a UTI-100C quadrupole mass spectrometer (QMS), a variable leak valve for introducing adsorbate molecules into the system, and instruments for Auger electron spectroscopy and Ar-ion sputtering. The BaTiO$_3$ sample was mounted at the end of a differentially pumped UHV translator. The sample holder was constructed from tantalum foil (0.025 mm thick), and it consisted of a square section to wrap around the back and edges of the sample and four parallel arms extending from the corners. The sample holder was spot welded across two power leads at the end of the translator, and the sample was heated by sending dc current through the sample holder from a computer-controlled power supply. The sample temperature was monitored with a K-type thermocouple attached to the back of the crystal with a ceramic adhesive (Aremco Products). A 3 mm hole was cut into the back of the sample holder to allow for the attachment of the thermocouple. In order to minimize the desorption signal from the support hardware during TPD measurements, the sample was positioned in front of a sample-sized hole in a quartz shield surrounding the QMS analyzer head.

Three different sets of annealing conditions were used to prepare the crystal surface prior to TPD measurements: (1) $T=1000$ K with 8 × 10$^{-8}$ torr oxygen for 30 min; (2) $T=800$–950 K for 4 h in UHV ($p=5×10^{-9}$ torr or lower while annealing); (3) $T=800$ K with 5 × 10$^{-7}$ torr oxygen for 1 h. After each annealing step, TPD measurements were performed separately with methanol (Alfa Aesar, Semiconductor Grade) and carbon dioxide (Matheson, 99.99%). Additional TPD measurements were performed on the vacuum-annealed surface with ammonia (Matheson, 99.99%), methylamine (Sigma-Aldrich, ≥98%), and pyridine (Fisher Chemical, Certified ACS). Adsorbate exposure was measured in Langmuir (L) units, where 1 L is equivalent to 10$^{-6}$ torr s. Before leaking the adsorbate molecules into the chamber, the gas supply line was purged repeatedly to minimize contamination. In addition, the methanol and pyridine were purified by several freeze-pump-thaw cycles. In the present study, TPD data were recorded over a temperature range of 300–850 K while heating the sample at a rate of 1 K/s.

III. RESULTS AND DISCUSSION

Table I lists the species present in the desorption spectra of each probe molecule, along with desorption peak temperatures ($T_p$). The estimated desorption activation energies ($E_d$) have been calculated from the Redhead equation, assuming first-order desorption kinetics and a pre-exponential factor of 10$^{33}$ s$^{-1}$. Desorption peaks were not observed in the ammonia, methylamine, or pyridine TPD data, indicating that detectable amounts of these molecules did not adsorb on the vacuum-annealed surface at room temperature. The exposures for these three molecules ranged from 10 to 30 L.

The three annealing steps were accompanied by changes in the color of the BaTiO$_3$ sample from light yellow after annealing step 1, to green after step 2, and back to light yellow again after step 3. We can infer from these color changes that the sample was reduced by annealing in UHV and then partially reoxidized when annealed with O$_2$.

Figure 1 shows TPD spectra obtained from the BaTiO$_3$(001) surface after each of the three annealing steps.

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2. L14
for methanol exposures of 25 L. The desorption signals of CH₃OH (m/e=31) and three reaction products, which are identified as CH₂O (m/e=29), H₂O (m/e=18), and CO (m/e=28), are plotted separately. On all three surfaces, the CH₃OH signal produces a broad desorption feature with two major peaks at 380 and 560 K (labeled A and B, respectively). However, the amplitude of these peaks is greatest in curve 2, indicating that more methanol adsorbed on the reduced surface as compared with either of the oxidized surfaces. One explanation for this effect is that the reduced surface contains a higher concentration of oxygen vacancies, which serve as adsorption sites for methanol at room temperature. Similar changes in peak amplitude are also observed in the desorption signals of CH₂O, H₂O, and CO, indicating that oxygen vacancies are also active sites for methanol decomposition.

In previous methanol TPD studies on related oxide surfaces (TiO₂, SrTiO₃, and polycrystalline BaTiO₃), methanol desorption above room temperature, as observed here on BaTiO₃(001), has generally been attributed to the recombinative desorption of methoxide species. For example, Kim and Barteau studied methanol decomposition on various
Table I. Summary of TPD products and peak temperatures for various probe molecules on BaTiO$_3$(001).

<table>
<thead>
<tr>
<th>Probe molecule</th>
<th>Desorbing species</th>
<th>$T_p$ (K)</th>
<th>$E_d$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (CH$_3$OH)</td>
<td>CH$_3$OH</td>
<td>380</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>560</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>590</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>CH$_2$O</td>
<td>625</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>625</td>
<td>170</td>
</tr>
<tr>
<td>Carbon dioxide (CO$_2$)</td>
<td>CO$_2$</td>
<td>360</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>720</td>
<td>197</td>
</tr>
<tr>
<td>Ammonia (NH$_3$)</td>
<td>None</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Methylamine (CH$_3$N)</td>
<td>None</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Pyridine (C$_5$H$_5$N)</td>
<td>None</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

Figure 2 shows TPD spectra obtained from the BaTiO$_3$(001) surface with 50 L exposures of carbon dioxide after annealing the crystal under the following conditions: (2) $T=800$–950 K in UHV for 4 h; (3) $T=800$ K with $5 \times 10^{-7}$ torr O$_2$ for 1 h. A linear background subtraction was applied to these desorption curves.

single crystal TiO$_2$(001) surfaces, including the Ar-ion sputtered surface and {011}- and {114}-facetted surfaces, using TPD and XPS.\textsuperscript{33} Low-temperature (365–375 K) and high-temperature (580–625 K) CH$_3$OH desorption peaks (analogous to peaks A and B in Fig. 1) were observed on all three surfaces. The low-temperature peak on the Ar-ion sputtered surface was attributed to molecularly adsorbed methanol, but in all other cases both peaks were due to the recombative desorption of methoxides. Therefore, we believe that methanol adsorbs dissociatively at oxygen vacancy sites on the BaTiO$_3$(001) surface at room temperature and forms methoxide species. Peaks A and B in the CH$_3$OH desorption signal in Fig. 1 are assigned to the recombative desorption of methoxides. The desorption of CH$_2$O, H$_2$O, and CO shown respectively producing two peaks at 360 and 720 K

on the oxygen-annealed surface. In contrast, peak D, which is the dominant peak on the reduced surface, is significantly smaller on the oxidized surface. This suggests that only the high-temperature peak should be attributed to CO$_2$ adsorbed at oxygen vacancies. The low-temperature peak may be due to CO$_2$ adsorbed at step edges or stoichiometric sites.

TPD measurements on single crystal TiO$_2$(110) (Refs. 39–41) and SrTiO$_3$(100) (Ref. 42) indicate that CO$_2$ interacts weakly with these surfaces, desorbing well below 300 K from both five-coordinate Ti$^{4+}$ and oxygen vacancy sites on TiO$_2$ and from stoichiometric Ti$^{4+}$ sites on SrTiO$_3$. Higher desorption temperatures have been observed, however, in TPD studies performed from room temperature on single crystal TiO$_2$(110) (Ref. 43) and the {011}-facetted surface of TiO$_2$(001).\textsuperscript{44} Interestingly, in these two cases (Refs. 43 and 44) the CO$_2$ desorption activation energies were 96 and 92 kJ/mol, respectively, which is in agreement with the desorption energy associated with the low-temperature CO$_2$ peak on BaTiO$_3$(001) (see Table I). This agreement may be a coincidence, or it may indicate that CO$_2$ can have a similar adsorption mechanism on stoichiometric TiO$_2$ and BaTiO$_3$ surfaces at room temperature. [CO$_2$ can adsorb on stoichiometric oxide surfaces at cation or anion sites in a variety of bonding configurations, but theoretical studies have indicated that while CO$_2$ adsorbs preferentially at cation sites on various TiO$_2$ surfaces,\textsuperscript{45,46} it prefers oxygen anion sites on BaO(100),\textsuperscript{47} BaTiO$_3$(001),\textsuperscript{48} and both SrO- and TiO$_2$-terminated SrTiO$_3$(001) surfaces.\textsuperscript{49} In addition, a dramatic increase in the chemisorption energy of CO$_2$ on SrTiO$_3$(100) is observed at oxygen vacancy sites induced by Ar-ion sputtering, resulting in a TPD peak at 650 K.\textsuperscript{42} This is consistent with the assignment of peak D in Fig. 2 to CO$_2$ adsorbed at oxygen vacancies. (It should be noted that CO
was also detected in CO$_2$ TPD on the reduced SrTiO$_3$ surface but has not been detected presently on BaTiO$_3$.) It is also interesting to compare the desorption energies corresponding to peaks C and D in Fig. 2 with chemisorption energies obtained by density functional theory (DFT) calculations for CO$_2$ adsorbed on SrTiO$_3$(001). DFT calculations indicate values of ~1 eV (96 kJ/mol) for CO$_2$ adsorbed at oxygen surface sites and 2.1 eV (203 kJ/mol) for oxygen vacancy sites, which are in agreement with the corresponding values in Table I. This agreement with theory supports the assignment of the low- and high-temperature CO$_2$ desorption peaks for BaTiO$_3$(001) to CO$_2$ adsorbed at oxygen and oxygen vacancy sites, respectively.

IV. CONCLUSION

The interactions of various molecules with the single crystal BaTiO$_3$(001) surface have been characterized by temperature programmed desorption. The surface was exposed to each TPD probe molecule at room temperature after annealing the crystal under oxidizing or reducing conditions to change the concentration of surface oxygen vacancy defects. The TPD spectra of NH$_3$, CH$_3$N, and C$_2$H$_4$N were flat, indicating that detectable amounts of these molecules did not adsorb at room temperature. Methanol and carbon dioxide both produced repeatable TPD spectra, which showed multiple desorption states and reaction products for methanol and low- and high-temperature desorption states for CO$_2$. The amount of adsorbed methanol was greater for the reduced surface than for the oxidized surfaces, indicating that methanol adsorbs and reacts at oxygen vacancies. For carbon dioxide, only the high-temperature peak showed an increase in magnitude on the reduced surface, indicating that the high-temperature state corresponds to CO$_2$ adsorbed at oxygen vacancies. The low-temperature peak may be attributed to CO$_2$ adsorbed at oxygen anion sites or other nonvacancy defects such as step edges.

This TPD study confirms earlier indications that methanol and CO$_2$ adsorb on BaTiO$_3$ surfaces at oxygen vacancy sites, and it indicates the temperature range over which these adsorption interactions are stable. The information contained in Table I may be useful in guiding future studies involving adsorption on BaTiO$_3$ or similar materials. In addition, the correct identification of molecular adsorption sites is an important component of the current effort to understand the mechanism by which polarization affects the surface chemical reactivity of barium titanate and other ferroelectric materials.

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