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The effect of ferroelectric polarization on the interaction of water and methanol with the surface of $LiNbO_3(0001)$

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ABSTRACT

Water and methanol temperature programmed desorption (TPD) measurements were performed on the positive (c^+) and negative (c^-) surfaces of poled ferroelectric lithium niobate ($LiNbO_3$) single crystals. The results indicate that the molecule–surface interactions are both coverage and polarization-dependent. From a comparison of the TPD spectra for the positive and negative surfaces, it is shown that the desorption temperatures of water and methanol are consistently lower on the negative surface by 15 K and 20 K, respectively. The TPD spectra were simulated using the Polanyi–Wigner equation with a coverage-dependent energy term. These calculations show that the polarization dependence of the desorption temperature is due to a difference in the zero-coverage desorption energies on the two surfaces equal to a few kJ per mole. The mechanism for the polarization effect is explored with *in situ* pyroelectric voltage measurements, which indicate that a surface voltage of ±2 mV develops in the $LiNbO_3(0001)$ samples during TPD measurements. The magnitude of the pyroelectric-induced surface charge is heating rate dependent.

1. Introduction

Ferroelectric materials are a special class of polar materials that exhibit both piezoelectricity and pyroelectricity, as well as electro-optic activity, high relative permittivity, and a positive temperature coefficient of resistivity (PTCR). These properties make them useful in a range of applications such as infrared sensors [1], MEMS devices [2], capacitors [3], optical modulators [4,5], and ferroelectric electron emitters [6]. Ferroelectric materials are unique because their internal spontaneous polarization (P_s) can be switched with an applied electric field. This effect is the basis of some nonvolatile memory devices in which a switchable ferroelectric thin film is used as the dielectric in a capacitor (FRAM) or as the gate oxide layer in a field-effect transistor (MFSFET) [7].

There have been several observations of polarization-dependent electronic and chemical surface phenomena in ferroelectric materials. These include significant changes in surface conductivity upon polarization switching [8], differences in the threshold energy for photoelectron emission from c^+ and c^- domains [9], and thermally stimulated electron emission due to the pyroelectric effect [10]. With regard to chemical reactivity, several studies have demonstrated that the chemical etch rate of ferroelectric compounds in acid solutions depends on the polarization direction at the crystal surface [11–13]. Inoue and colleagues have also shown that polarization affects the catalytic and adsorptive properties of metal and semiconducting thin films deposited on a ferroelectric support [14,15]. Ferroelectric materials also exhibit interesting polarization-dependent photochemical properties, which have been demonstrated by the spatially selective oxidation and reduction of metal ions at the surface of multidomain ferroelectric substrates, when illuminated with ultraviolet (UV) light [16,17]. Furthermore, it has been shown that photochemical deposition reactions can be combined with local control of ferroelectric polarization to drive the assembly of surface nanostructures [18].

Recently, various experiments have been done to better understand the physical mechanisms behind polarization-dependent surface properties in ferroelectric materials, particularly in regard to the interactions of particles and molecules with poled surfaces. The experiments include detailed studies of the photochemical deposition of metal nanoparticles [19–23], the deposition of charged particles [24–26], and the adsorption and reaction of molecules on ferroelectric surfaces [27–32]. As a result of this work, it has been shown that the mechanisms behind the observed polarization effects generally involve charge transfer processes and/or electrostatic forces induced by space charge layers and band bending, external screening charges on the surface, and in some cases the pyroelectric properties of the ferroelectric substrate. In addition, differences in the atomic surface structure of oppositely poled surfaces should be considered [33–36]. The contribution of each of

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these elements depends on the properties of the ferroelectric substrate, such as the electronic carrier density, band gap, thickness, and the presence of defects and domain boundaries, as well as the experimental conditions, including the light source used for carrier excitation, the substrate temperature, and whether the experiment is performed in a solution, air, or vacuum environment.

In the present work, the interactions of water and methanol molecules with the c^+ and c^- surfaces of lithium niobate ($LiNbO_3$ or LN) crystals have been studied using temperature programmed desorption (TPD) in an ultrahigh vacuum (UHV) environment. The desorption kinetics have been analyzed in order to quantify the effect of polarization on desorption energy. In order to examine the role of the pyroelectric effect in TPD measurements and to study screening charge relaxation kinetics at the surface of $LiNbO_3$, pyroelectric measurements have been performed in UHV. Recent work by Yun et al. [27,28] has shown that polar molecules (2-propanol and acetic acid) desorb at temperatures approximately 100 K higher from the c^+ surface of $LiNbO_3$. A comparative study with non-polar probe molecules indicates that this effect may be due to electrostatic interactions between the ferroelectric surface and the molecular dipole. In addition, the work of Bharath et al. [30] provides evidence that the assembly of liquid crystal molecules at the c^+ and c^- $LiNbO_3$ surfaces through vapor deposition is also influenced by similar electrostatic interactions. Recent work has shown that polarization can also affect the sticking coefficients [29,31] and reaction activation energy [32] of molecules adsorbed on ferroelectric surfaces.

2. Experimental procedures

Fully poled, optical grade, $LiNbO_3(0001)$ single crystals grown by the Czochralski method (congruent composition) were purchased from MTI Corporation. The crystals were 1 mm thick, polished on both sides, and cut into 5 × 5 mm squares. The crystals were *z*-cut, meaning that the *c* axis (the ferroelectric axis) was oriented perpendicular to the crystal surface. A pyroelectric measurement was performed on each crystal to determine the direction of the spontaneous polarization [37]. The crystal was placed on a polished copper plate, and the top surface of the crystal was gently contacted to an aluminum foil electrode. The voltage across the crystal was measured with a voltmeter while it was heated with a heat gun. As in other studies, we defined the c^+ or *positive* face as the one that registered a negative pyroelectric voltage and the c^- or *negative* face as the one that registered a positive voltage [10,27,28]. Two LN samples were used in the experiments: one to study the positive surface and another to study the negative surface.

TPD measurements were performed in a UHV chamber with a UTI-100C quadrupole mass spectrometer (QMS), an electron gun and cylindrical mirror analyzer detector for Auger electron spectroscopy, a sputter ion gun, and a leak valve for dosing adsorbate molecules into the system. The LN sample was mounted at the end of a differentially pumped UHV translator, which could be filled with liquid nitrogen to cool the sample below room temperature. The sample holder was a 5 × 5 mm square of tantalum foil (0.25 mm thick) with four parallel arms spot welded to the corners. The arms were made from thinner tantalum foil (0.025 mm thick) and were 12 mm long and 0.8 mm wide. To attach the LN sample to the holder, both surfaces were coated with indium and then pressed into contact while using a heat gun to soften the indium. Mounting with indium provides very good thermal contact between the sample and the holder [38,39]. The arms of the sample holder were then spot welded to two stiff copper power leads at the end of the translator. While in vacuum, the LN sample was heated by sending DC current through the sample holder with a computer-controlled power supply. The sample temperature was monitored with a K-type thermocouple attached to the side of the crystal with a zirconia-based ceramic adhesive (Aremco Products). Prior to TPD measurements, the samples were thoroughly degassed by annealing in UHV for 1 h at 725 K. TPD was then performed at a base pressure of approximately 1×10^{-10} torr. The QMS is fitted with a quartz shield containing a circular aperture. The sample was positioned in front of the aperture during TPD to block out species desorbing from the support hardware and to enhance the sensitivity of the detector to species desorbing from the sample surface. For the TPD measurements discussed here, the samples were cooled to 155 K before adsorbate exposure and then heated to 450 K at a rate of 1 K/s.

Water and methanol TPD measurements were performed separately on both the positive and negative samples. Adsorbate exposure was controlled by leaking water or methanol (both purified by several freeze-pump-thaw cycles) into the chamber at a partial pressure of 2×10^{-10} torr. The time of exposure ranged from 0 to 2500 s, and the total exposure was calculated in Langmuir (L) units, where 1 L is equivalent to 10^{-6} torr-s. For methanol exposures, the sample was placed near the end of a tube extending from the leak valve, which increased the exposure by a factor of approximately 2.5 compared with the amount that the crystal receives when positioned away from the tube. For water exposures, the sample was turned away from the tube. The adsorbate exposures ranged from 0.01 to 0.74 L for water and 0.05–1.3 L for methanol. These values include contributions from the background.

Pyroelectric measurements similar to those described above were also performed in vacuum using the setup shown in Fig. 1. During the measurements, the sample was moved into contact with a copper electrode and heated by passing DC current through a tungsten filament positioned 1.5 mm behind the sample holder. The filament was used as an alternative heating method because passing current directly through the sample holder generated a significant amount of noise in the measured voltage signal. In order to prevent charging effects due to electrons emitted from the filament, the sample holder was grounded and the electrode wire was shielded coaxially with copper foil. Additional high frequency noise filtering was achieved by placing a 0.1 μF capacitor between the measurement leads outside of the UHV chamber. This configuration provided a repeatable way to measure the pyroelectric voltage of the sample while varying conditions such as the starting temperature, the heating rate, and the residual gas pressure.

3. Results and discussion

Several mass-to-charge ratios (m/e) were monitored during the TPD measurements. The relative intensities of the m/e signals in the TPD spectra were the same as the molecular cracking patterns of water and methanol, indicating that the adsorbates desorbed molecularly from both surfaces. In Fig. 2 the desorption spectra of water and methanol on the positive and negative $LiNbO_3(0001)$ surfaces are compared. Only the signal for the primary m/e of each molecule is plotted in Fig. 2 ($m/e = 18$ for water; $m/e = 29$ for methanol).

Fig. 2a compares the TPD spectra of water on the positive and negative surfaces for a range of exposures. On both surfaces, there is a single desorption feature with a peak temperature that gradually decreases from ~270 to 200 K, as the exposure is increased. The desorption peak is broad and has a trailing edge that extends up to approximately 350 K. At each exposure level, the desorption peak temperature for the negative surface is about 15 K lower than that for the positive surface, suggesting that there is a systematic difference in the desorption kinetics for the positive and negative surfaces. In addition, the peaks from the negative surface are smal-