I. INTRODUCTION

Oxide materials exhibit a wide range of physical behavior, including superconductivity, magnetoresistance, and ferroelectricity. 

Strontium titanate (SrTiO3) is an especially interesting and technologically important oxide, due to its unique structural and dielectric features. SrTiO3 has a cubic perovskite structure at room temperature and undergoes a phase transition to a tetragonal structure at 105 K. Unlike other perovskite oxides, pure, unstressed SrTiO3 does not transform into a macroscopic ferroelectric phase. However, the addition of impurities or the application of stress results in ferroelectricity.

Because of its structure, SrTiO3 is a desirable substrate for high temperature, superconducting thin films. Its large dielectric constant and high breakdown strength make it a useful material in electronic devices. It is also a promising wide bandgap (3.3 eV) semiconductor with potential optical applications. The recent demonstration of high-mobility heterostructure devices with superior operating characteristics illustrates the potential of SrTiO3 as a substrate for future electronic technologies.

Hydrogen is an omnipresent impurity in oxides, including SrTiO3, and is a potential source of n-type conductivity. Despite the prevalence of hydrogen, very little is known about its fundamental interactions with native defects such as vacancies. In addition to affecting electrical properties, these interactions play a role in proton conduction in perovskite oxides, an important issue in fuel cells. In as-grown SrTiO3, isolated hydrogen forms a bond with a host oxygen, resulting in an infrared (IR) absorption band near 3500 cm⁻¹ due to the O–H bond-stretching vibration. Experiments and theory suggest that the O–H bond is aligned along the line that connects oxygen neighbors. In ZnO, Raman spectroscopy has shown that hydrogen can form interstitial H₂ molecules, with different frequencies corresponding to the H₂, HD, and D₂ isotope combinations. Additionally, IR spectroscopy has shown that hydrogen can passivate zinc vacancies. The O–H bonds that are formed lead to characteristic vibrational frequencies, with well-defined isotope shifts. When samples are exposed to a mixture of hydrogen and deuterium, new lines corresponding to HD complexes appear. These new lines provide unambiguous evidence that the complex contains two hydrogen atoms.

II. EXPERIMENT

In this paper, we report the results of an IR absorption study of SrTiO3 annealed in hydrogen and/or deuterium. We used nominally undoped SrTiO3 single crystals from MaTeck GmbH. For hydrogen and/or deuterium doping, the crystal was annealed at 800 °C in a sealed silica ampoule that was filled with 1/2 atm H₂ and/or D₂ gas. The annealing was performed in a horizontal tube furnace for 45 min and was terminated by quenching the ampoule to room temperature in water. In order to study the stability of the O–H complexes, a series of isochronal anneals was performed at temperatures from 300 to 1100 °C. Each anneal had a duration of 30 min and was carried out in the open air. IR absorbance spectra were recorded after each annealing temperature step.

Mid-IR absorption spectra were obtained with a Bomem DA8 vacuum Fourier transform infrared spectrometer equipped with a globar light source, a KBr beam splitter, and a liquid-nitrogen-cooled indium antimonide (InSb) detector. The spectral range was 1800–7000 cm⁻¹ and the instrumental resolution was 1.0 and 0.2 cm⁻¹ for room-temperature and low-temperature measurements, respectively. A Janis closed-cycle helium cryostat system was used to maintain the samples at low temperatures.

III. RESULTS AND DISCUSSION

Figure 1 shows the IR absorbance spectra at 10 K for a SrTiO3 sample after annealing in hydrogen and/or deuterium...
at 800 °C. In the hydrogen-annealed sample (top spectra), two absorption peaks at 3355 and 3384 cm\(^{-1}\) are observed. Also shown are the previously reported absorption peaks around 3500 cm\(^{-1}\), which are associated with O–H bond stretching modes. The ratio of H\(_I\) to H\(_{II}\) peak areas varied from sample to sample, suggesting that H\(_{II}\) involves a defect, the concentration of which is sample-dependent. From the areas of the O–H peaks,\(^{22}\) we estimate the IR-active H concentration to be in the 10\(^{16}\)–10\(^{17}\) cm\(^{-3}\) range.

When hydrogen is substituted by deuterium, the two “new” peaks are red-shifted to 2489 and 2510 cm\(^{-1}\), respectively. The frequency ratios of the hydrogen- and deuterium-related peaks are 1.35, which is close to the value expected for a harmonic oscillator consisting of a hydrogen (deuterium) atom bound to an oxygen atom,

\[
\sqrt{\mu_{\text{OD}}/\mu_{\text{OH}}} = 1.37,
\]

where \(\mu_{\text{OH}}\) and \(\mu_{\text{OD}}\) are the reduced masses of the O–H and O–D units, respectively. When the sample is annealed in a mixture of hydrogen and deuterium, two additional peaks at 3373 and 2499 cm\(^{-1}\) are observed. No extra peaks are observed near the region of the 3500 and 2592 cm\(^{-1}\) peaks. These observations indicate that the new absorption peaks (at 3355 and 3384 cm\(^{-1}\)) and the previously reported peaks (around 3500 cm\(^{-1}\)) originate from two different defects. The LVMs around 3500 cm\(^{-1}\) belong to a defect containing one hydrogen atom, whereas the LVMs at 3355 and 3384 cm\(^{-1}\) are due to two equivalent hydrogen atoms. In this paper, these defects are labeled H\(_I\) and H\(_{II}\), respectively.

The LVMs of a deuterated SrTiO\(_3\) sample are displayed as a function of temperature in Fig. 2. At low temperatures, the absorption peaks split, due to the reduction in symmetry as the crystal transforms from the cubic to the tetragonal phase. As shown in Fig. 2(a), the H\(_I\) defect absorption peak splits into three components below the transition temperature (\(\sim 105\) K).\(^{2,3}\) The H\(_{II}\) defect also shows a splitting of the O–H peaks, but the magnitude is much less [Fig. 2(b)]. A Lorentzian fit to one of the H\(_{II}\) bands reveals that it splits into three components [Fig. 2(c)]. Figure 2(a) also shows that the LVMs of the H\(_I\) defect shift upward in frequency as the temperature decreases. In contrast, the LVMs of the H\(_{II}\) defect [Fig. 2(b)] show a negligible shift in frequency, suggesting a weaker perturbation by the surrounding host atoms. This points toward the involvement of a vacancy,\(^{23}\) where the open volume reduces the effect of the lattice on the O–H LVMs. A strontium vacancy is the most likely candidate because it is a double acceptor, making it energetically favorable for two H atoms to give their electrons to the neighboring oxygen atoms and form O–H bonds. Therefore, we propose that the H\(_{II}\) defect is a strontium vacancy passivated by two hydrogen atoms.

To account for the splitting of the O–H LVMs (Fig. 2), we introduce a model where each hydrogen atom is bound to a nearest-neighbor oxygen atom and directed toward the strontium vacancy (Fig. 3). In Fig. 3 there are three possible configurations for the two H atoms. At high temperatures, these configurations are equivalent due to the cubic symmetry of the crystal structure, resulting in two absorption peaks corresponding to the symmetric (3355 cm\(^{-1}\)) and antisymmetric (3384 cm\(^{-1}\)) normal modes. At low temperatures, there is a lowering of the symmetry of the structure due to the rotation of the oxygen octahedra about the c axis, and the three configurations are no longer equivalent. This accounts for the temperature-induced splitting observed in the LVMs (Fig. 2).

FIG. 1. IR absorption spectra measured for SrTiO\(_3\) samples at 10 K after annealing in H\(_2\) (top), D\(_2\) (middle), and a mixture of H\(_2\)+D\(_2\) (bottom) at 800 °C. Spectral resolution is 1 cm\(^{-1}\).

FIG. 2. (Color online) Temperature dependence of the LVM frequencies of (a) H\(_I\) and (b) H\(_{II}\) defects of deuterated SrTiO\(_3\). (c) Lorentzian fitting of one of the H\(_{II}\) absorption bands at 10 K showing three overlapping peaks. Spectral resolution is 0.2 cm\(^{-1}\) at lower temperatures (\(\leq 110\) K).

FIG. 3. (Color online) Proposed model of the H\(_{II}\) defect: a strontium vacancy passivated by two hydrogen atoms.
for the triplet splitting of the H\textsubscript{II} peaks. As the tetragonal phase is actually polycrystalline, the relative intensities of the split peaks varied somewhat from run to run, due to the random distribution of domains.

In Fig. 4, the results of the isochronal annealing experiments on hydrogenated SrTiO\textsubscript{3} samples are shown. At each step, the IR absorbance spectra were recorded at 220 K and the integrated absorbance was calculated for each peak. Figure 4 provides evidence that H\textsubscript{I} and H\textsubscript{II} defects do not have the same origin, as they exhibit different thermal kinetics. The results also confirm that the H\textsubscript{II} LVMs (the 3355 and 3384 cm\textsuperscript{-1} peaks) belong to the same defect, as they retain the same relative intensity regardless of the annealing temperature. The increase in H\textsubscript{II} population near 400 °C suggests that there is a reservoir of “hidden hydrogen” that is IR-inactive. At temperatures greater than 400 °C, these hydrogen atoms are released from the reservoir, forming O–H bonds that are observable in the IR.

To probe this phenomenon further, we performed isochronal annealing on a hydrogen-annealed sample that was subsequently deuterated. Figure 5 shows the absorption spectra obtained at 200 K for each annealing step. Before annealing the sample in air, an absorption spectrum of the sample was obtained (bottom), which shows deuterium-related peaks. The lack of hydrogen peaks implies that, upon deuteration, the deuterium atoms displaced the hydrogen atoms from their sites. However, when the sample was annealed at 400 °C, a weak H-related peak appeared. At 500 °C, the H-related peak became strong and HD peaks emerged. At higher temperatures, the D-related peaks disappeared, leaving only H-related peaks. These observations are consistent with our model of hidden hydrogen in the crystal that becomes mobile at 400 °C.\textsuperscript{24} These hydrogen atoms overwhelm the deuterium atoms, completely displacing them at 600 °C.

An obvious question is: what is the identity of the hidden hydrogen? It has been found that, in ZnO, hidden hydrogen exists in the form of hydrogen H\textsubscript{2}. The H\textsubscript{2} vibration has a weak dipole moment such that it has not been detected by IR absorption,\textsuperscript{25} but has been observed by Raman scattering.\textsuperscript{20} Assuming that the same is true for SrTiO\textsubscript{3}, annealing the sample at temperatures from 400 to 700 °C dissociates the H\textsubscript{2}, and the liberated H are trapped before they can diffuse out of the sample. The trapped hydrogen atoms form IR active O–H defects and enhance the H\textsubscript{I} peaks. The dissociation temperature of 400 °C is similar to that for H\textsubscript{2} molecules in ZnO.\textsuperscript{25} Further annealing at higher temperatures causes these H-related peaks to decay as hydrogen diffuses out of the sample (Fig. 4).

IV. CONCLUSIONS

In summary, we have observed a hydrogen-related defect in SrTiO\textsubscript{3}, which we attribute to a strontium vacancy passivated by two hydrogen atoms. The results of isochronal annealing experiments suggest the presence of a hidden hydrogen species, possibly H\textsubscript{2}. It is noteworthy that in ZnO, a much less ionic crystal, hydrogen passivates zinc vacancies\textsuperscript{21} and forms H\textsubscript{2} molecules.\textsuperscript{22,25} Our observations therefore suggest “universal behavior” of hydrogen in a diverse range of oxides.

ACKNOWLEDGMENTS

This work was supported by NSF Grant No. DMR-1004804 and DOE Grant No. DE-FG02-07ER46386. We thank Susanne Stemmer, Anderson Janotti, and Chris Van de Walle (University of California, Santa Barbara) for helpful discussions.

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