

## Ambient-temperature incorporated hydrogen in Nb:SrTiO<sub>3</sub> single crystals

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Electrolysis of water has been implemented to inject hydrogen into the SrTiO<sub>3</sub> single crystal doped with 1 wt % of Nb. Direct evidence of OH<sup>-</sup> group formation in the Nb:SrTiO<sub>3</sub> single crystal has been obtained by Fourier-transform infrared (FTIR) analysis, showing an intensity increase of the absorption at a wave number of about 3500 cm<sup>-1</sup>. FTIR analysis also revealed lattice relaxation due to hydrogen doping. High-resolution x-ray diffraction (XRD) analysis further illustrated lattice expansion, as evidenced by the left shift of the SrTiO<sub>3</sub> (200) peak for the hydrogen doped sample. The decrease in the XRD rocking curve linewidth of this (200) peak for the hydrogen-doped sample suggested that hydrogen doping relaxed the local constraints in the crystal. In contrast to the usual great increase in conductivity of insulating perovskite oxides by hydrogen doping, an obvious decrease in conductivity of the highly conductive Nb:SrTiO<sub>3</sub> single crystal was observed after hydrogen doping. © 2003 American Institute of Physics. [DOI: 10.1063/1.1574842]

In recent years, much attention has been paid to the reactions and impact of hydrogen on perovskite ferroelectric oxides. Even though perovskite oxides are widely used in ceramic capacitors and piezoelectric devices, the reaction between hydrogen and (Ba,Sr)TiO<sub>3</sub> or Pb(Zr,Ti)O<sub>3</sub> thin film capacitors during forming gas annealing (FGA) and the consequent degradation is a major obstacle to their integration as nonvolatile memories in complementary metal-oxide-semiconductor based devices.<sup>1,2</sup> Chen and co-workers recently found that the ambient temperature reaction of atomic hydrogen generated by electrolysis of water causes serious problems of reliability in (Ba,Sr)TiO<sub>3</sub> and Pb(Zr,Ti)O<sub>3</sub>.<sup>3,4</sup> To date, extensive studies have been carried out to determine the mechanism of FGA degradation and the following fairly clear picture has been obtained: hydrogen incorporated into perovskite lattice as a shallow donor results in a great increase in leakage currents and an obvious depression in polarization. However, fundamental studies and in-depth understanding of the ambient-temperature reaction between atomic hydrogen and perovskite oxides are still limited.

In this letter, we report direct evidence of the ambient-temperature incorporation of hydrogen in Nb doped SrTiO<sub>3</sub> single crystals (Nb:SrTiO<sub>3</sub>) and its impact on the conductivity and structure of the crystals. SrTiO<sub>3</sub> is a typical perovskite oxide. Its single crystals are widely used as a substrate or buffer layer for ferroelectric films and high-*T<sub>c</sub>* superconducting films deposition, due to their similarities in structure. Nb:SrTiO<sub>3</sub> single crystals are especially attractive as they are highly conductive and therefore can be simultaneously used as substrate and bottom electrode material for the growth of ferroelectric films. Their high conductivity is also very useful for the present investigation. In studies of dielectric ceramics, metal electrodes usually have to be used in electrolysis of water experiments. The electrode effect, particularly the interface effect, may sometimes shadow what happened in

the dielectric materials. By contrast, the Nb:SrTiO<sub>3</sub> single crystal itself can be used as the cathode to electrolyze water and hydrogen can be deposited on them directly. Therefore, the electrode problem can be avoided and the reaction between hydrogen and perovskite-type oxides can be studied without influence of any other arbitrary effects.

A commercial product of (100) oriented 1 wt % Nb-doped SrTiO<sub>3</sub> single crystals that had been cut into size of 10×5×1 mm<sup>3</sup> were mirror polished and immersed in a 0.01 M NaOH solution at 25 °C. The crystals were then connected to the negative electrode of a 4.5 V dc voltage while the counter electrode was connected to the positive side. The single crystals were highly conductive. Electrolysis of water thus occurred due to the applied dc voltages and hydrogen was evolved on the surface of the crystals while oxygen was evolved on the counter electrode. This treatment is referred to as “hydrogen charging” hereafter. In this report, the Nb:SrTiO<sub>3</sub> single crystal was treated for 20 h and the cathodic current density was 0.3 mA/cm<sup>2</sup>. The dc voltage was removed after the treatment and the crystal was taken out, cleaned, and dried. In order to study the effects of hydrogen charging, the Nb:SrTiO<sub>3</sub> single crystal before hydrogen charging (hereafter called the “control sample”) and after hydrogen charging (hereafter called the “H doped sample”) were subjected to electrical conductivity measurements, Fourier-transform infrared (FTIR) analysis and x-ray diffraction (XRD) analysis. FTIR absorption spectra were obtained with a Nicolet’s Magna-TRTM 750 FTIR spectrometer. The structures of the crystals were examined using a high-resolution XRD (Bruker D8 Discovery x-ray diffractometer). The beam was monochromized and collimated by a four-bounce (220) Ge monochromator. Only Cu Kα<sub>1</sub> radiation with a nominated wavelength of 0.154 060 nm was thus used in the experiments. Both  $\theta$ -2 $\theta$  scans and  $\theta$  rocking curves were recorded with angular resolutions of 0.001°.

The FTIR absorption spectra for the control and H doped samples are shown in Figs. 1 and 2. One can see that for the H doped sample the absorption around the wave number of

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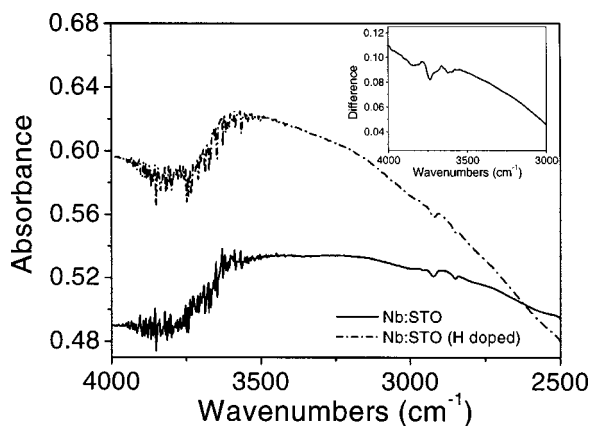


FIG. 1. FTIR absorption spectra of the control and H doped Nb:SrTiO<sub>3</sub> in the range of 2500–4000 cm<sup>-1</sup>. The inset shows the difference between the two spectra (after smoothing) revealing the existence of a hump at a wave number of about 3500 cm<sup>-1</sup>.

3500 cm<sup>-1</sup> increased, as shown in Fig. 1. A wave number of 3500 cm<sup>-1</sup> is a characteristic absorption for OH<sup>-</sup> group; therefore, the formation of the OH<sup>-</sup> group in the H doped sample can be illustrated. This is direct evidence showing that H can be injected into perovskite lattice at an ambient temperature by means of the electrolysis of water. The evolution of hydrogen on the surface of Nb:SrTiO<sub>3</sub> single crystals when dc voltages were applied can be written as<sup>5</sup>



where H<sub>ads</sub> represents an adsorbed hydrogen atom. Since atomic hydrogen is highly reactive, we believe it was atomic hydrogen that diffused into the Nb:SrTiO<sub>3</sub> single crystal and formed OH<sup>-</sup> groups with oxygen atoms in the crystal.<sup>6</sup> The same reactions by hydrogen molecules can only be accomplished at elevated temperatures.<sup>7</sup>

The doping of hydrogen in our experiment contrasts with an earlier report by Waser,<sup>8</sup> in which no solubility was found in donor-doped SrTiO<sub>3</sub> by the hot water vapor method, as oxygen vacancy is needed when hydrogen is doped in the form of a H<sub>2</sub>O molecule

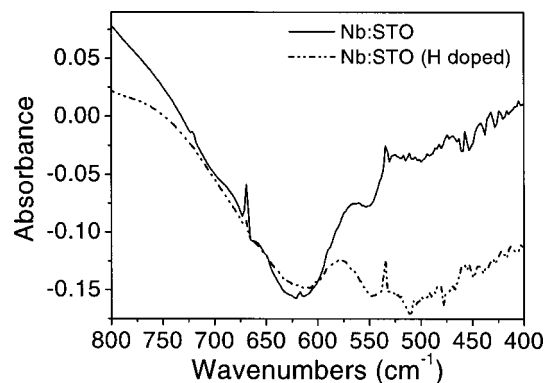


FIG. 2. FTIR absorption spectra of the control and H doped Nb:SrTiO<sub>3</sub> in the wave number range of 400–800 cm<sup>-1</sup>.

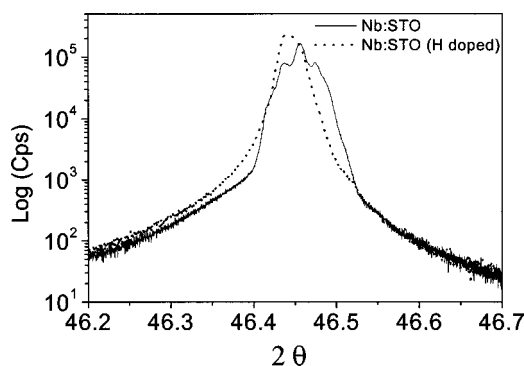


FIG. 3. XRD spectrum of  $\theta$ - $2\theta$  scan showing SrTiO<sub>3</sub> (200) peaks for the control and H doped Nb:SrTiO<sub>3</sub>.

where H<sub>i</sub><sup>+</sup> represents an ionized hydrogen in interstitial site. In this letter, hydrogen was doped in the form of atomic hydrogen; thus no oxygen vacancy is needed



Although hydrogen is in interstitial site, it forms an O–H bond with nearby oxygen so the characteristic absorption for the OH<sup>-</sup> group can be observed.

Figure 2 shows the IR absorption spectra in the 400–800 cm<sup>-1</sup> range. Based on earlier reports,<sup>9</sup> the diffused absorption peak at about 470 cm<sup>-1</sup> corresponds to the LO modes of the SrTiO<sub>3</sub> structure, and the peak at 530 cm<sup>-1</sup> corresponds to the TO modes. The scattered absorption peaks of the TO and LO modes in the control sample are due to the screening effect by the Nb doping induced charge carries to the internal electric field. By contrast, the softening and linewidth decrease of the LO and TO absorption peaks for the H doped sample suggest a decrease in numbers of charge carriers.<sup>10–12</sup> It is worth noting that, for the control sample, there are three small shoulders in the peak corresponding to the Ti–O stretching modes at 570–585 cm<sup>-1</sup>, while there is only a single peak at 580 cm<sup>-1</sup> for the hydrogen doped sample.<sup>13</sup> This indicates that H doping may relax the Ti–O bonds and the crystal lattice. Also, one can see that for the H doped sample the peaks at 670 and 725 cm<sup>-1</sup>, which may correspond to the Nb–O stretching modes, disappeared or significantly decreased.<sup>14</sup> The Nb atom is known to replace the Ti atom as the donor doping; therefore the change in Ti–O and Nb–O stretching vibrations suggests that the presence of the H atom and the OH<sup>-</sup> group may change the bonding states of Ti–O and Nb–O.

The relaxation of the crystal structure was further illustrated by a high-resolution XRD analysis. Figure 3 shows the SrTiO<sub>3</sub> (200) XRD peaks of a  $\theta$ - $2\theta$  scan for the control and H doped samples. For the control sample, the SrTiO<sub>3</sub> (200) peak splits into three small peaks, suggesting that the sample may consist of domains with a slight difference in their lattice constants as a result of the lattice distortion by the incorporation of Nb atoms into SrTiO<sub>3</sub>. These domains have structures that deviate slightly from the perfect cubic structure and possibly possess twinning. The left shift of the SrTiO<sub>3</sub> (200) peak for the H doped sample indicates lattice expansion due to the presence of interstitial H in the lattice. As reported earlier, the expansion of the lattice due to H doping can be understood by considering the two physical effects.<sup>15</sup> First, the H atom is charged positively, and owing

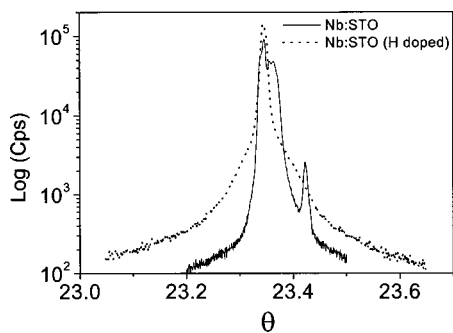


FIG. 4. XRD rocking curve of the  $\text{SrTiO}_3$  (200) peaks of the control and H doped  $\text{Nb:SrTiO}_3$ .

to the Coulomb interaction, the Sr and Ti atoms move outwards. Second, the insertion of H atoms is accompanied by the creation of chemical bonds between the H and O atoms; thus the chemical bonds between Ti–O and Sr–O are weakened, leading to the outward displacement of these atoms.

Unexpectedly, the H doped sample shows only one sharp (200) peak, suggesting a uniform expansion of the crystal lattice into a perfect cubic structure without twinning. This feature was also reflected in the XRD rocking curves of the (200) peaks for the control and H doped samples as shown in Fig. 4. The rocking curve for the (200) diffraction from the control sample shows a series of peaks indicating that the domains are tilted with respect to each other. By contrast, the rocking curve for the (200) diffraction from the H doped sample shows only a single peak with strong diffused scattering. This confirms the idea of a uniform expansion of crystal lattice into a perfect cubic structure by H doping. The strong diffused scattering is evidence of a high concentration of point defects introduced by the H doping. It can be concluded that H doping relaxed the local constraints in the crystal.

The impact of H doping on the electric properties was studied by measuring the resistivity of the control and H doped samples. The control and H doped samples were coated with dot electrodes with a diameter of  $1.0 \text{ mm}^2$  for each dot. The spacing between each dot was 2.0 mm. The average resistance between each two-electrode pair was about  $4.0 \Omega$  for the control sample and about  $40 \Omega$  for the H doped sample, respectively. It is assumed that hydrogen is in interstitial sites and free electrons are formed so the resistivity is greatly decreased in hydrogen degraded insulating perovskite oxides. Nb is a well-known donor dopant in  $\text{SrTiO}_3$ ; therefore H doping in  $\text{Nb:SrTiO}_3$  is supposed to generate more charge carrier electrons and further reduce resistivity. However, the results showed that H doping in the  $\text{Nb:SrTiO}_3$  single crystal increased the resistivity by about one order,

indicating that hydrogen has a different effect on highly conducting perovskite oxides than it does on insulating perovskite oxides. Based on the change in the Ti–O and Nb–O stretching modes as illustrated in Fig. 2, we assume that H doping may result in the formation of Nb–(OH) bonds and reduce the mobility of charge carrier electrons, thus increasing resistivity. An in-depth understanding of the increased resistivity is still not clear at this moment, and further investigation is highly desirable.

In summary, direct evidence of H doping in the  $\text{Nb:SrTiO}_3$  single crystal by means of the electrolysis of water has been obtained by FTIR analysis. FTIR analysis also revealed  $\text{Nb:SrTiO}_3$  crystal lattice relaxation due to H doping. A high-resolution XRD analysis further illustrated lattice expansion due to the presence of H, evidenced by the left shift of the  $\text{SrTiO}_3$  (200) peak. An XRD analysis also revealed that H doping relaxed the local constraints in the crystal. The incorporated hydrogen in the  $\text{Nb:SrTiO}_3$  caused the resistivity to greatly increase, and the mechanism needs further study.

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