Effects of hydrogen anneals on oxygen deficient $SrTiO_{3-x}$ single crystals

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The influence of hydrogen gas anneals on the electrical properties of nominally undoped, oxygen-deficient $SrTiO_{3-x}$ single crystals was investigated. Titanium getter layers and vacuum anneals were used to obtain oxygen-deficient $SrTiO_{3-x}$ with a low electrical resistivity. These crystals showed an optical absorption peak at 2.92 eV and strong midinfrared absorption. Subsequent anneals at 800 °C in forming gas, which contained 10% hydrogen, returned the crystals into the insulating, transparent state. The mechanisms by which hydrogen anneals can compensate for the effects of oxygen vacancies in $SrTiO_{3-x}$ are discussed. The results show that forming gas anneals of stoichiometric $SrTiO_3$ can lead to complex electrical conduction behavior. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2969037]

Oxygen vacancies can act as electron donors in $SrTiO_3$, causing a wide range of phenomena, including superconductivity.[1] They are also believed to form relatively easily during thin film deposition even at moderate growth temperatures.[2,3] Electrically conducting $SrTiO_3$ crystals are often obtained by annealing in highly reducing, hydrogen-containing atmospheres.[4–6] The use of hydrogen as a reducing agent makes establishing the relationship between oxygen vacancies and the electrical properties complicated. In particular, interstitial hydrogen has been suggested to act as a shallow donor in $SrTiO_3$ and related materials.[7,8] Thus both oxygen vacancies and hydrogen may potentially contribute to the electrical conductivity of $SrTiO_3$. Understanding the role of hydrogen in $SrTiO_3$ is also of technical importance. Forming gas, which contains hydrogen, is used in semiconductor device processing and causes a large increase in the leakage current of $SrTiO_3$ films and related materials, such as $(Ba,Sr)TiO_3$.[9,10] Infrared (IR) studies of $SrTiO_3$ heated in humid atmospheres (which thus contain an oxidant) have established that hydrogen is incorporated interstitially where it bonds to the lattice oxygen to form hydroxide (OH^-).[11–13] In contrast, less is known about the role of hydrogen in reducing conditions and in the presence of oxygen vacancies.

In this letter, we report on a series of annealing studies of nominally undoped $SrTiO_3$ single crystals aimed at separating the role of oxygen vacancies and hydrogen on the electrical conductivity. We show that hydrogen anneals effectively compensate for the electrical and optical properties caused by large concentrations of oxygen vacancies in $SrTiO_{3-x}$.

Double-side polished, Verneuil-grown, nominally undoped $SrTiO_3$ single crystals (MaTeck GmbH, Germany) were annealed in different atmospheres. An ultrahigh vacuum chamber ($\sim 10^{-9}$ torr) was used for vacuum anneals at 800 °C for 30 min using ramp up and down rates of 10 °C/min. On selected samples, either a Ti backing layer ($\sim$500 nm) or patterned Ti top contacts were deposited by electron beam evaporation before the vacuum anneals. Oxygen and forming gas ($10\%H_2/90\%N_2$) anneals were carried out in a rapid thermal annealing furnace at 1150 and 800 °C, respectively. In each case the ramp-up time was 20 s followed by rapid cooling, all carried out in the same atmosphere. Electrical resistivities were characterized by four-point-probe measurements using Ti top contacts deposited through a shadow mask. Backside secondary ion mass spectroscopy (SIMS) profiling using 6 kV CsX+ primary ions was used to investigate compositional changes in the Ti backing layer after vacuum annealing. Optical transmittance measurements at wavelengths between 350 and 2600 nm were recorded using a Shimadzu UV-3600 spectrophotometer. The study of OH-related peaks, located around 3500 cm^{-1} in the IR, was carried out using a Nicolet Magna 850 spectrometer.

No measurable electrical conductivity was observed for the as-received and oxygen-annealed crystals or those annealed in vacuum without Ti backing layer or contacts. $SrTiO_3$ crystals with a Ti back layer that were annealed in vacuum showed a low sheet resistance (1 Ω/sq) and their color changed to black. Figure 1 shows a SIMS depth profile for oxygen and titanium across the Ti/$SrTiO_3$ interface before and after vacuum annealing. The Ti film contained significant amounts of oxygen after annealing, in particular near the interface with $SrTiO_3$. Thus the electrical conductivity of $SrTiO_{3-x}$ was directly related to large concentrations of oxygen vacancies produced by the oxygen gettering properties of the Ti back layer. Annealing of $SrTiO_3$ crystals with patterned Ti top contacts also resulted in a low sheet resistance

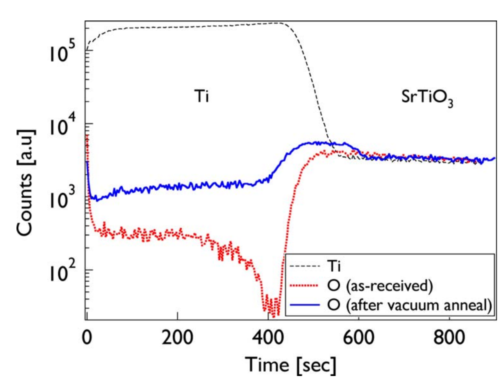

FIG. 1. (Color online) SIMS oxygen depth profiles across a Ti/$SrTiO_3$ interface before and after annealing in vacuum. The Ti profile is also shown to identify the layers. Note the accumulation of oxygen in the Ti film, especially near the interface with $SrTiO_3$, after the vacuum anneal.

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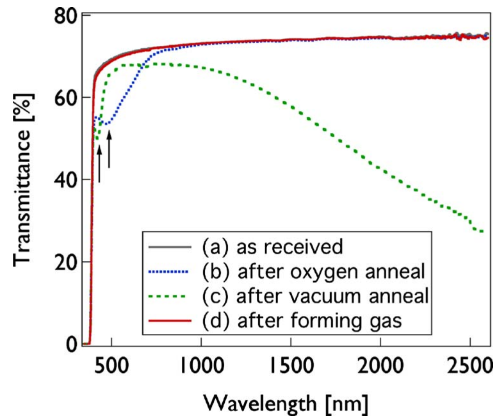

FIG. 2. (Color online) Optical transmittance as a function of wavelength for a $SrTiO_3$ single crystal labeled (a)–(d) in the order of annealing treatments: (a) as received $SrTiO_3$, (b) after an oxygen anneal at 1150 °C, (c) after depositing Ti top contacts and annealing in vacuum at 800 °C for 30 min, and (d) after a 20 s forming gas anneal at 800 °C. The arrows indicate absorption peaks after annealing in oxygen and vacuum, respectively.

(75 Ω/sq), corresponding to a resistivity of 3.75 Ω cm, and grayish color. Next, the conducting $SrTiO_{3-x}$ crystals were annealed in forming gas for 20 s. This anneal returned the samples into an insulating, colorless, and transparent state.

Figure 2 shows optical transmission spectra between 350 and 2600 nm of the same $SrTiO_3$ crystal subjected to successive annealing treatments. The as-received crystal showed no absorption peaks in this wavelength range [Fig. 2(a)]. Oxygen anneals caused light brown color accompanied by an absorption peak at 2.62 eV with a wide shoulder [Fig. 2(b)]. Oxygen deficient $SrTiO_{3-x}$ obtained by Ti gettering showed a strong absorption in the mid-IR range [Figs. 2(c) and 3(b)]. The strength of this absorption is known to scale with the charge carrier concentration[14–16] and was thus consistent with the electrical conductivity of the crystals. In addition, an absorption peak at 2.92 eV (424 nm) was observed [see Fig. 2(c)]. This peak also appeared after forming gas anneals (~80 s) of as-received samples (discussed below). Annealing $SrTiO_{3-x}$ crystals in forming gas for 20 s removed the mid-IR absorption band (consistent with the crystals becoming insulating) and the peak at 2.92 eV [Fig. 2(d)]. The optical transmission in the visible to mid-IR range was similar to that of the as-received crystal. The same result was obtained if the Ti layers were removed before the forming gas anneal.

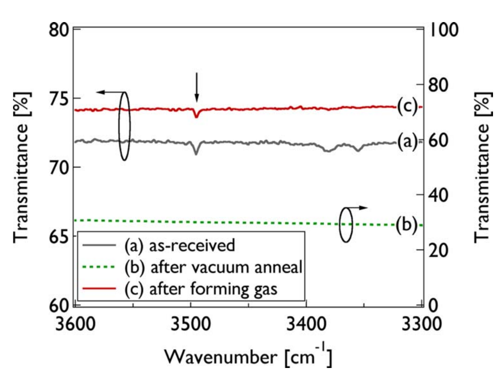

FIG. 3. (Color online) IR transmittance as a function of wave number for a $SrTiO_3$ single crystal labeled (a)–(c) in the order of annealing treatments: (a) as received $SrTiO_3$, (b) after depositing Ti top contacts and annealing in vacuum at 800 °C for 30 min, and (c) after a 20 s forming gas anneal at 800 °C. Note the scale is different in (b). The vertical arrow indicates the OH related peak.

Figure 3 shows IR transmission spectra containing peaks characteristic for OH around 3500 cm^{-1}.[11–13] The as-received crystal [Fig. 3(a)] showed an OH peak, which could be removed by annealing in oxygen (not shown) and by vacuum anneals with Ti contacts or back layers [Fig. 3(b)]. The OH peak reappeared after the 20 s forming gas anneal [Fig. 3(c)]. It was, however, reduced in strength and lacked the satellite peaks at smaller wave numbers that were present in the as-received sample. Further annealing in forming gas caused the OH peak to disappear (not shown). SIMS analysis showed that hydrogen was present in both forming gas and vacuum annealed samples without OH peaks.[17]

In summary, hydrogen anneals had two major effects on electrically conducting, oxygen deficient $SrTiO_{3-x}$: they removed optical absorption peaks, which were present in both oxidized and oxygen deficient samples, and returned the crystals into an insulating state. Even nominally undoped $SrTiO_3$ single crystals are known to contain impurities, such as Fe and Al, and typical purity levels are no better than 99.99%.[18] Iron on the Ti site can possess multiple valence states, which produce optical absorption peaks.[4,6,19–21] Oxidizing anneals stabilize higher Fe valence states, while reducing anneals can stabilize Fe in lower valence states to compensate for oxygen vacancies, which can also form complexes with the Fe. A peak at 2.9 eV has previously been observed in reduced, Fe-doped $SrTiO_3$, but has not yet been assigned to a specific defect (complex).[4,6,21] The results show that hydrogen has a bleaching effect on these color centers. Such a procedure is apparently employed for some commercial, Verneuil-grown $SrTiO_3$ single crystals, which as-grown are dark in color and are made insulating and transparent by Ar/H_2 anneals.[22] A possible explanation is that the hydrogen anneal causes a change in the Fermi level and transformation to Fe^{3+}, which has no optical absorption peak.[20,21,23]

With respect to the mechanism by which hydrogen anneals eliminate the electrical conductivity, it is unlikely that highly reducing forming gas anneals reoxidize $SrTiO_{3-x}$. One possible explanation is that traps for the charge carriers are generated. These traps could involve impurities or native defects present in the samples; for example, $Fe^{3+}-V_O$ complexes are electron traps.[24] The formation of traps would be consistent with observations reported in the literature that hydrogen anneals reduce the conductivity of donor (Nb) doped $SrTiO_3$ crystals by an order of magnitude.[25] Further investigations are, however, required to determine the specific point defects (complexes) present before and after the forming gas anneal and their charge states. Future studies should also address how hydrogen is incorporated in oxygen deficient $SrTiO_{3-x}$. The reduction/removal of OH peaks may simply be due to the oxygen deficiency, causing fewer binding sites to be available for interstitial hydrogen; however, recent experiments of hydrogen ion conduction in Fe-doped $SrTiO_3$ under very reducing conditions have suggested that hydrogen may also be substituted on the oxygen vacancy site as hydride ion.[26]

Finally, the results show that the influence of hydrogen anneals on the conductivity of oxygen-stoichiometric $SrTiO_3$ is expected to depend on the relative kinetics of competing processes. The highly reducing atmosphere can create oxygen vacancies, but their effect on the electrical properties may be passivated by the hydrogen anneal. A complex behavior was indeed observed: forming gas anneals of oxidized $SrTiO_3$ (no Ti contacts) showed the onset of decrease in the mid-IR transmittance after annealing for some time ($\sim$200 s) and the sample became electrically conductive. However, additional forming gas anneal brought the sample back to the insulating, colorless, transparent state. The significance of kinetics was also reported by Wild *et al.*, who observed that slow cooling in hydrogen atmosphere resulted in insulating $SrTiO_3$.[6] The behavior appears to be unique to $SrTiO_3$ (and possibly related materials). Conducting, oxygen deficient TiO_{2-x} crystals obtained using Ti getter layers remained conductive after forming gas anneals.

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