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Heavy Interstitial Hydrogen Doping into $SrTiO_3$

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We achieve the introduction of an extremly large amount of interstitial hydrogen into strontium titanate ($SrTiO_3$) by low-temperature hydrogen ion beam irradiation. The *in situ* transport measurements reveal an unprecedented thermal hysteresis of the resistivity.

Interstitial or substitutional chemical doping is the most conventional method to control the electronic states of materials. For example, superconductivity has been observed in fullerenes by interstitial doping of alkali metals (K, Rb, Cs),[1] and in cuprates and iron pnictides by chemical substitutions.[2] In particular, hydrogen doping is expected to be a powerful method to drastically change the physical properties of materials.[3] Composed of an electron and a proton, hydrogen is the simplest, smallest and lightest element, and because of its medium electronegativity among the elements, it shows a variety of charged states from −1 (hydride, H^-) to +1 (proton, H^+).[3a] Thus, hydrogen may interact significantly with materials with minimum perturbation to the lattice. For example, switchable optical properties in yttrium and a reversible phase modulation in VO_2 were observed by hydrogen introduction.[3b,c]

Strontium titanate ($SrTiO_3$) is one of the most important and widely studied material among perovskite oxides (ABO_3) in terms of fundamental and applied sciences. While the native $SrTiO_3$ is a band insulator, chemically substituted ones exhibit a variety of physical properties including metallicity and superconductivity in Nb-doped $SrTiO_3$, ferroelectricity by oxygen isotope exchange and photocatalytic ability under visible light in Rh-doped $SrTiO_3$.[4] Besides the conventional chemical substitution, interstitial hydrogen doping can change the physical properties of $SrTiO_3$. First-principles calculations have suggested that the interstitial hydrogen in $SrTiO_3$ acts as a shallow donor (Fig. 1a),[5] and a shallow hydrogen-like muonium state in $SrTiO_3$ was observed by a muon spin rotation experiment.[6] However, the effects of interstitial hydrogen on physical properties have not been studied well. Although a few papers reported interstitial hydrogen doping into $SrTiO_3$ by annealing under hydrogen or humid atmosphere, the hydrogen concentration was quite small (10^{16}–10^{17} cm^{-3}).[7] These methods may also generate a large amount of oxygen vacancy which act as an electron donor.[18,21] Therefore, the role of interstitial hydrogen on the physical properties of $SrTiO_3$ remains unclear.

Recently, we developed a new apparatus for low-energy (≤5 kV) and low-temperature hydrogen ion (H_2^+) beam irradiation with *in situ* resistivity measurements.[8] In the ion beam method, hydrogen ions are accelerated by applying a voltage, and are physically introduced into materials, where the amounts of hydrogen doping can be easily controlled by irradiation time. Previously, a few papers reported changes in the optical properties of $SrTiO_3$ by high-energies (60 kV, 3 MV, 9 MV) H^+ irradiations at room temperature.[9] However, low-energy irradiation is preferable for minimizing irradiation damage. Moreover, the introduced hydrogen might be partially desorbed from the sample at room temperature.

Herein, we report the achievement of heavy interstitial hydrogen doping (10^{21} cm^{-3}) into insulating $SrTiO_3$ films by low-energy and low-temperature H_2^+ irradiation. The hydrogen desorption was suppressed significantly at low temperatures, allowing heavy interstitial hydrogen doping and precise study of the doping effects. A metallic conductivity was observed by irradiation at 300 and 150 K, and the latter gave rise to significantly lower resistivity than the former. The *in situ* transport measurements revealed an unforeseen thermal hysteresis loop in the resistivity induced by low-temperature irradiation at 50 K, indicating highly effective interstitial hydrogen doping at low temperatures and partial hydrogen desorption at high temperatures.

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Epitaxial thin films of $SrTiO_3$ of 100 nm thickness were fabricated on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) (001) substrates by pulsed laser deposition. Out-of-plane and in-plane φ-scan X-ray diffraction (XRD) measurements confirmed epitaxial growth of the films (Fig. S1). The as-grown samples were highly insulating (>10 MΩ). Hydrogen ion was irradiated onto the films with an acceleration voltage of 5 kV at 300, 150 and 50 K.

The resistivity of the $SrTiO_3$ films under the H_2^+ irradiations at 300 and 150 K is shown in Fig. 1b. We observed a large decrease in the resistivity of $SrTiO_3$ film by irradiation at 300 K. The resistivity decreased rapidly with the initial hydrogen ion dose. Subsequent irradiation induced a further gradual decrease in resistivity, and then the resistivity was saturated under the heavy dose. The large decrease in resistivity indicates the injection of charge carriers by the hydrogen introduction. Finally, the metallic conductivity of the film was successfully observed down to 130 K after irradiation at 300 K (Fig. 1c). A larger decrease in resistivity and a lower saturation resistivity under the heavy dose were observed by the lower-temperature irradiation at 150 K (Fig. 1b). Indeed, compared at the same irradiation dose, the resistivity after irradiation at 150 K was about one order of magnitude smaller than that after irradiation at 300 K (Fig. 1c). These results strongly indicate that the low-temperature irradiation enables heavy hydrogen doping of $SrTiO_3$ by suppressing hydrogen desorption. The averaged hydrogen concentration of the film was calculated from the irradiation dose at 150 K, provided that all the irradiated hydrogen atoms remain in the film (Fig. 1b). For example, the total ion dose of 3.4×10^{16} ions cm^{-2} corresponds to a nominal value of $x = 0.43$ ($H_{0.43}SrTiO_3$).

Fig. 2a shows the temperature dependences of the resistivity after 150 K irradiations. For $x = 0.03$–0.08, H_xSrTiO_3 exhibited a metallic behaviour at high temperatures, and a crossover to semiconducting behaviour at low temperatures indicating electron localization. Such a localization of electrons at low temperatures has been observed in cation (A or B site)-substituted or oxygen-deficient perovskite oxides, and was attributed to the disorder in the perovskite structure.[10] In the present case, the localization is likely caused by the grain boundaries in the pristine film and/or some disorders induced by the doped hydrogen atoms and possible irradiation damage. It should be mentioned that the $SrTiO_3$ film after irradiation at 150 K maintained the perovskite structure as confirmed by *ex situ* XRD measurements (Fig. S2). Above $x = 0.13$, a metallic conductivity was observed down to 4 K. We note that no thermal hysteresis was observed in Fig. 2a.

The $SrTiO_3$ film irradiated at 150 K exhibited an irreversible increase in resistivity when heated up to 300 K (Fig. 2b). After 150 K irradiation, the film showed normal metallic behaviour from 4 to 180 K. However, the resistivity abruptly increased above 180 K during heating (red curve in Fig 2b). After the heating to 300 K, the resistivity became almost comparable with that after 300 K irradiation (10^{-2} Ω cm, Fig 1b), and slightly increased with time (dotted line, Fig. 2b). When the film was cooled again down to 4 K (blue curve in Fig. 2b), the metallic behaviour was still observed, although the resistivity remained relatively high. The most probable origin of the irreversible behaviour is the partial desorption of interstitial hydrogen from $SrTiO_3$ above 180 K. We also considered the possibility of formation of electrically inactive interstitial H_2 molecules by heating to 300 K. However, first-principles calculations reported that interstitial H_2 has much higher formation energy than interstitial hydrogen (H_i).[5a] Therefore, it is unlikely that the irreversible increase in resistivity is caused by the formation of interstitial H_2. As discussed later, the heavy interstitial hydrogen doping into the $SrTiO_3$ film was achieved by irradiation at 300 K, and the low-temperature irradiation at 150 K enabled a larger amount of interstitial hydrogen to remain in the sample than irradiation at 300 K.

To evaluate the residual amount of hydrogen in the film irradiated at 150 K, *ex situ* secondary ion mass spectrometry (SIMS) was performed at room temperature. The dynamic SIMS depth profiles of H, Ti, O and Al ions in the H-doped $SrTiO_3$/LSAT film are shown in Fig. 3. The secondary ion intensity of Ti drastically decreased at 100 nm, corresponding to the interface between the $SrTiO_3$ film and the LSAT substrate. This is also supported by a drastic increase in Al signals at 100 nm. We also observed a sharp peak in the hydrogen concentration at 100 nm, possibly because of trapped hydrogen atoms at the interface. The film contains a large amount of hydrogen (10^{21} cm^{-3}) although there is a certain distribution with depth caused by the ion beam irradiation. The average hydrogen concentration was estimated as $x = 0.14 \pm 0.06$. This concentration is substantially smaller than that estimated from the irradiation dose ($x = 0.43$) at 150 K, which confirms partial hydrogen desorption from $SrTiO_3$ after subsequent heating to 300 K.

After irradiation at 300 K (2×10^{16} ions cm^{-2}, Fig. 1b), we cooled the sample (blue open circles in Fig. 4a) and further irradiated hydrogen at 50 K. The additional low-temperature irradiation induced a further decrease in the resistivity (green arrow in Fig. 4a, and Fig. S5). When cooled down to 4 K after 50 K irradiation, the resistivity showed almost temperature independent behaviour. On subsequent heating up to 300 K, the resistivity decreased above 70 K and started to increase rapidly above 180 K, and returned to nearly the initial value at 300 K (red open circles in Fig. 4a). It is well reproduced by a second irradiation at 50 K (closed circles in Fig. 4a). Thus, an unforeseen thermal hysteresis loop was observed with the irradiation at 50 K and subsequent heating to 300 K. The low-temperature irradiation and subsequent heating above 180 K correspond to hydrogen introduction and partial desorption, respectively.

Fig. 4b displays the temperature dependence of resistivity after 50 K irradiation. The resistivity showed an unusual decrease above ca. 70 K, accompanied by another hysteresis behaviour: the resistivity remained low even when cooled again down to 4 K. It is likely that the trapped electrically inactive hydrogen atoms (H^0) start to migrate above ca. 70 K and act as a shallow donor. In $SrTiO_3$, interstitial hydrogen partially desorbed above 180 K. Therefore, irradiation at 150 K enabled the effective carrier injection via heavy interstitial hydrogen doping. Here, we explain that interstitial hydrogen is heavily doped into $SrTiO_3$ by hydrogen ion irradiation. It is well known that perovskite oxides are proton conductors at high temperatures, and hydrogen in perovskite oxides generally exists as an interstitial proton (H^+).[12] In some cases, hydrogen can substitute for the oxygen anion (O^{2-}) in transition metal oxides as the hydride ion (H^-).[13] Recently, it has been reported that the oxyhydrides $ATiO_{3-x}H_x$ (A = Ba, Sr, Ca) exhibit various properties with good stability up to 380–460 °C under inert atmospheres.[14] However, it is unlikely that the present hydrogen irradiated $SrTiO_3$ is an oxyhydride. After low-temperature irradiation, the resistivity of the $SrTiO_3$ films irreversibly increased above 180 K (Fig. 2b and 3a). This corresponds to partial desorption of doped hydrogen above 180 K. It is reported that the H_2 release occurs in the oxyhydrides $ATiO_{3-x}H_x$ (A = Ba, Sr, Ca) at a much higher temperature (650–730 K) than in the present system (180 K).[14b] Therefore, the hydrogen irradiated $SrTiO_3$ is not an oxyhydride. Additionally, first-principles calculations indicated that the hydrogen atom hardly substitute the oxygen atom in $SrTiO_3$ because of its high formation energy.[5c] It should be mentioned that if hydrogen ion irradiation introduced substantial amount of substitutional hydrogen, repeated irradiations would monotonically decrease the resistivity of $SrTiO_3$ film, which is inconsistent with the observed hysteresis loop in Fig. 4a. Therefore, the thermal hysteresis behaviour is a strong evidence showing that the most of irradiated hydrogen atoms does not substitute oxygen anion. We cannot rule out the possible generation of oxygen vacancy by the irradiation. However, the reproducible thermal hysteresis cannot be explained by the oxygen vacancy because the sample was kept under vacuum during the experiment. We also observed a slight lattice expansion (Δc = 0.004 Å) after irradiation at 150 K (Fig. S2), which was consistent with introduction of interstitial hydrogen. The c-axis (3.9599(8) Å) increased relative to that before irradiation (3.9559(7) Å). In contrast, a slight lattice shrinkage was observed in the oxyhydride $ATiO_{3-x}H_x$ film (Δc = −0.008 Å).[14c] Therefore, the lattice expansion after irradiation suggests that the doped hydrogen exists as interstitial hydrogen in $SrTiO_3$. Therefore, we conclude that low-energy H_2^+ irradiation induced a substantial amount of interstitial hydrogen in $SrTiO_3$.

The decrease in resistivity is attributable to n-type doping via interstitial hydrogen in $SrTiO_3$, which was confirmed by *ex situ* Hall effect measurements (Fig. S6). The Hall coefficients for the $SrTiO_3$ film after 150 K irradiation are negative, indicating that the major carriers in the film are electrons. We also confirmed heavy carrier doping into $SrTiO_3$ (nearly 10^{20} cm^{-3}) even after partial hydrogen desorption. The resistivity after irradiation at 150 K is one order of magnitude lower than that after subsequent heating to 300 K as shown in Fig. 2b. Therefore, the carrier density after irradiation at 150 K is considered to be one order of magnitude larger than 10^{20} cm^{-3}, provided that the mobility does not change.

The resistivity of the $SrTiO_3$ film displayed saturation behaviour during irradiation at 300 K (Fig. 1b). By subsequent irradiation at 50 K, further decrease in the resistivity was observed (Fig. S5(a)). Therefore, the saturation behaviour during irradiation at 300 K can be attributed to desorption of excess hydrogen from highly doped $SrTiO_3$, which indicates the importance of low-temperature irradiation for heavy interstitial hydrogen doping. In contrast, the migration of doped hydrogen atoms is probably hindered at low temperatures below 70 K (Fig. 4b). Therefore, choosing an appropriate irradiation temperature is important for highly effective carrier injection via heavy interstitial hydrogen doping into materials.

In conclusion, we have shown the heavy hydrogen doping (10^{21} cm^{-3}) into insulating $SrTiO_3$ films by low-energy (5 kV) hydrogen ion beam irradiation at low temperature. The film exhibited metallic conductivity after irradiation at 300 K. A larger decrease in resistivity was successfully observed by the lower-temperature irradiation at 150 K because of the suppression of hydrogen desorption. The heavy interstitial hydrogen doping was confirmed by SIMS analysis and by an unprecedented thermal hysteresis of the resistivity after irradiation. As hydrogen ion irradiation is applicable for any material of interest, the low-energy hydrogen ion irradiation at a suitable temperature could provide a facile and highly effective method for heavy interstitial hydrogen doping and for exploring new physical properties of materials.

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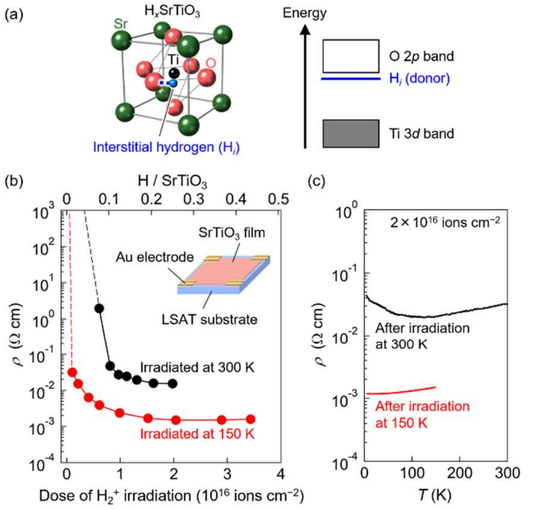

Fig. 1 (a) Schematic illustrations of crystal and electronic structures of H_xSrTiO_3. Green, black, red, and sky blue spheres, respectively, denote Sr, Ti, O, and H atoms. Interstitial hydrogen (H_i) in $SrTiO_3$ act as a shallow donor.[5,6] (b) Dose dependence of the resistivity of $SrTiO_3$ films by H_2^+ irradiation at 300 and 150 K. The dotted line serves as a visual guide and the inset shows the sample geometry. Averaged nominal hydrogen concentrations of the film after irradiation were calculated from the irradiation doses. (c) Temperature dependences of the resistivity of $SrTiO_3$ films after the irradiation at 300 K (black) and 150 K (red) at the same irradiation dose (2×10^{16} ions cm^{-2}).

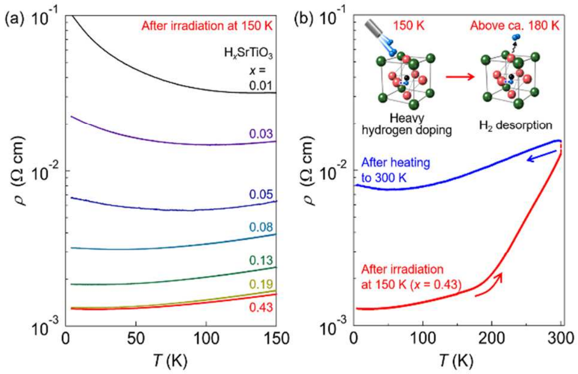

Fig. 2 (a) Temperature dependences of the resistivity of the $SrTiO_3$ film after the 150 K irradiations in Fig. 1b with various hydrogen concentrations (H_xSrTiO_3). Averaged nominal hydrogen concentrations of the film after irradiation were calculated from the irradiation doses. (b) Temperature dependence of the resistivity when heated up to 300 K after 150 K irradiation (x = 0.43) (red), and then cooled down to 4 K (blue). The red dotted line indicates an increase in the resistivity at 300 K with time (ca. 30 min). The inset illustrates the probable reason for the irreversible increase in resistivity.

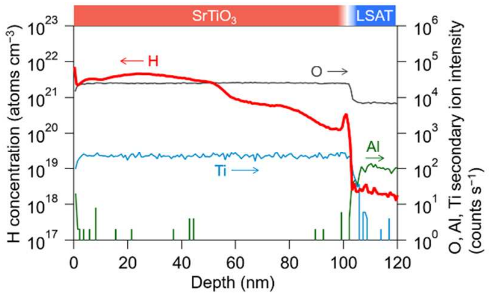

Fig. 3 Dynamic SIMS depth profiles of H, Ti, O, and Al secondary ions in the $SrTiO_3$/LSAT film after 150 K irradiation. The SIMS profiles were measured at room temperature. The secondary ion intensity of hydrogen was converted to hydrogen concentration by using a standard sample.

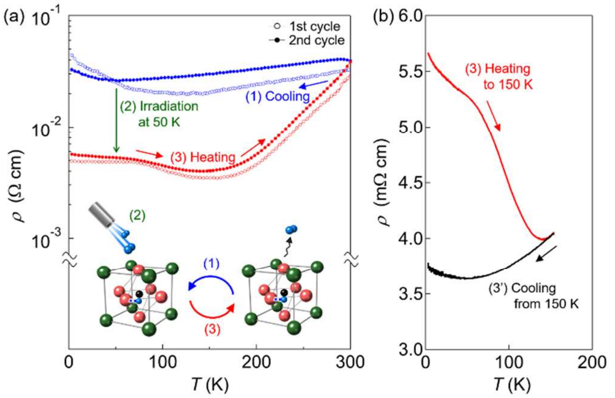

Fig. 4 (a) Temperature dependence of the $SrTiO_3$ film irradiated at 300 K measured before and after subsequent irradiations at 50 K. Open and closed circles correspond to first and second cycles of the hysteresis loop, respectively. The inset illustrates a probable mechanism of the hysteresis loops for the resistivity. Irradiations were performed at 50 K after cooling down to 4 K and heating up to 50 K. After the irradiation, the sample was cooled down to 4 K, and heated up to 300 K. (b) Temperature dependence of the resistivity when heated up to 150 K after irradiation at 50 K (red), and then cooled down to 4 K (black).