Long-range propagation of protons in single-crystal VO$_2$ involving structural transformation to HVO$_2$

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Vanadium dioxide (VO$_2$) is a strongly correlated electronic material with a metal-insulator transition (MIT) near room temperature. Ion-doping to VO$_2$ dramatically alters its transport properties and the MIT temperature. Recently, insulating hydrogenated VO$_2$ (HVO$_2$) accompanied by a crystal structure transformation from VO$_2$ was experimentally observed. Despite the important steps taken towards realizing novel applications, essential physics such as the diffusion constant of intercalated protons and the crystal transformation energy between VO$_2$ and HVO$_2$ are still lacking. In this work, we investigated the physical parameters of proton diffusion constants accompanied by VO$_2$ to HVO$_2$ crystal transformation with temperature variation and their transformation energies. It was found that protons could propagate several micrometers with a crystal transformation between VO$_2$ and HVO$_2$. The proton diffusion speed from HVO$_2$ to VO$_2$ was approximately two orders higher than that from VO$_2$ to HVO$_2$. The long-range propagation of protons leads to the possibility of realizing novel iontronic applications and energy devices.

Controlling the properties of strongly correlated electronic materials via carrier and impurity doping has gained significant attention over the past years. Doping has an impact on 3$d$-band filling, which often results in dramatic modification of the orbital states. This results in large changes of electronic properties, such as the metal-insulator transition (MIT). For example, a shift of the MIT temperature ($T_{\text{MIT}}$) of VO$_2$ via doping with a variety of elements, such as W, Mo, and Nb has been reported. This is caused by charge transfer from the impurity ions to the vanadium ions through the oxygen ions, which displaces an integral number of 3$d$ electrons in $V^{4+}$ that are Mott insulating states to $3d^{1+\delta}$, resulting in the formation of more stable metallic states. When using impurity elements with large atomic numbers of W, Mo and Nb, however, it is impossible to dynamically control the number of mobile carriers because of solid-state materials determined by an initial doping level. On the other hand, protons having strongly reductive activity in oxide materials can dynamically move via external fields and function as an electron donor. Recent work has demonstrated that dynamic proton-intercalation results in a large, reversible resistance modulation in oxide thin films, such as SrTiO$_3$, NdNiO$_3$, and VO$_2$ via a catalytic effect, a non-catalytic effect, or an electric field. In general, the intercalation of protons in the insulating VO$_2$ state decreases its resistivity and it approaches a metallic state with a pseudo rutile structure. According to Yoon et al., heavy doping with protons using Pt catalytic nano-particles transforms VO$_2$ into HVO$_2$ under an H$_2$ + Ar gas atmosphere. HVO$_2$ has a different crystal structure from the tetragonal VO$_2$, and it demonstrates typical-insulating behavior that follows the Arrhenius equation with a higher resistivity than that of VO$_2$. Moreover, a reversible structural deformation is possible between VO$_2$ in air and HVO$_2$ in the H$_2$ + Ar gas atmosphere. This reversible resistance change has the potential to lead to the realization of novel ionic and/or electronic applications. However, there is lack of information regarding essential physical parameters in this system, such as the diffusion constant of the intercalated protons in VO$_2$ and the crystal transformation energy between VO$_2$ and HVO$_2$.

In this work, we demonstrated the long-range propagation of protons in VO$_2$. This was accomplished by investigating the transient electronic transport properties during proton intercalation in VO$_2$ and the associated structural transformation to HVO$_2$ under H$_2$ + Ar gas atmosphere. This was followed by a return to VO$_2$ from HVO$_2$ after proton desorption under an N$_2$ gas atmosphere. The results showed that the diffusion constants and crystal transformation energies differed for the two states.

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Results

Device structures and basic transport properties. For VO₂ microwire devices prepared on TiO₂ (001) substrates, the width (w) was fixed at 2 μm and the distance between catalytic Pt electrodes (d) was from 2 μm to 10 μm, as shown in the schematic in Fig. 1a. The optical image on the right of Fig. 1a shows a VO₂ microwire for the proton intercalation experiment. Figure 1b shows the temperature dependence of the resistivity curves in a VO₂ microwire with d = 4 μm. The pristine VO₂ shows typical electronic transport properties with hysteresis due to the MIT in a N₂ gas atmosphere (solid black dots). Continuous annealing under H₂ (5%) + Ar (95%) gas at 380 K for ~5 h resulted in a marked change to the insulating phase that followed the Arrhenius equation (solid red dots). The resistivity increased by ~5 orders of magnitude, which is in agreement with ref. 13. They determined that the heavily hydrogenated VO₂ had a structural deformation to HVO₂, which resulted in a ~10% expansion in the [100] direction of the rutile VO₂ structure and opened a band gap calculated by a first-principle method. The band gap (Eg) of the hydrogenated HVO₂ was 0.71 eV, as derived from the inset of Fig. 1b using the equation as a pure semiconductor ln(σ) = -Eg/kₐT + ln(σ₀), where σ, σ₀, and kₐ are the conductivity of the thin film, a constant, and the absolute temperature, respectively.
and the Boltzmann constant, respectively. The $E_i$ takes the half value with the calculated bandgap of the HVO$_2$ with 2 electron doping unit cell in ref. 13. Furthermore, these results indicate that the VO$_2$ microwires also become fully hydrogenated VO$_2$ in the $4\mu$m gap between the Pt source and drain catalytic electrodes. Figure 1c shows the reversibility of the transport properties under H$_2$/Ar or N$_2$ gases at 380 K. The VO$_2$ microwire was initially metallic at 380 K in a N$_2$ atmosphere. As soon as H$_2$ gas was introduced into the measurement cell, the resistivity promptly increased with the intercalation of protons into VO$_2$. Eventually, the H$_2$ gas annealing resulted in the heavily hydrogenated VO$_2$, i.e., it formed the insulating HVO$_2$ phase. Compared with the time required for the transformation from VO$_2$ to HVO$_2$, the HVO$_2$ phase returned to the initial metallic VO$_2$ more quickly on N$_2$ gas annealing. This trend was in agreement with the data from ref. 13. The results of this experiment revealed the micro-scale diffusion of protons with a crystal change from VO$_2$ to HVO$_2$. Regarding repeatability of electronic property of VO$_2$ thin films after N$_2$ annealing at 380 K from HVO$_2$, the temperature dependence of resistance curves is almost same as the pristine curve, keeping the framework of VO$_2$ (Please see the section E in Supplementary Information in detail).

**Analysis of the transient resistance behavior.** Based on the H$_2$ or N$_2$ atmosphere dependent reversible reaction, the evolution of the proton concentration in VO$_2$ with time was investigated. As a boundary condition between the Pt and VO$_2$ interface, the chemical reaction rate as a differential equation with respect to time ($t$) was introduced according to:

$$\frac{dn_{\text{inter}}}{dt} = k_1n_{\text{H}^+} - k_2n_{\text{inter}}$$  \hspace{1cm} (1)

where $k_1$ and $k_2$ are the forward and reverse reaction rate constants, respectively, $n_{\text{H}^+}$ is the proton concentration at the contact area between the Pt catalytic electrodes and VO$_2$, and $n_{\text{inter}}$ is the proton concentration at the VO$_2$ interface. From Eq. (1), the behavior of Fig. 1c can be understood. In the beginning, protons are intercalated into VO$_2$, at the contact points between Pt, VO$_2$, and the H$_2$+Ar gas phase, as seen in an upper illustration of Fig. 2a, because $k_1n_{\text{H}^+} > k_2n_{\text{inter}}$ and $n_{\text{inter}} = 0$ during the initial stage. The value of $k_1n_{\text{H}^+}$ gradually approaches that of $k_2n_{\text{inter}}$, until the two values are finally equal and reach the equilibrium state. As the H$_2$+Ar gas is changed to N$_2$, $n_{\text{H}^+}$ approximately becomes zero, thus the protons in VO$_2$ are removed and the insulating HVO$_2$ returns to the metallic VO$_2$ form. This dynamic reaction at the interface was taken as a boundary condition with a dynamic time-dependence in the simulation below.

Next, we consider how the intercalated protons diffuse in VO$_2$. Theoretically, for ion diffusion, the ionic fluxes likely arise from a gradient in the ion concentration in the solid-state material. Thus, $n_{\text{HVO}_2}$ is the proton ratio in a VO$_2$ unit cell, namely, $\frac{dn_{\text{HVO}_2}}{\partial x} = -\frac{dn_{\text{HVO}_2}}{\partial x}$, which predicts the spatiotemporal evolution of the ion concentration. This with the following equation was obtained:

$$\frac{\partial n_{\text{HVO}_2}}{\partial t} = -D\frac{\partial^2 n_{\text{HVO}_2}}{\partial x^2}$$  \hspace{1cm} (2)

To evaluate the spatiotemporal evolution of the proton concentration in VO$_2$, numerical analysis using the finite difference method (FDM) was carried out based on the boundary condition of Eq. (1) and the transient diffusion equation of Eq. (2) (see Section A in Supplementary Information).

The inset of Fig. 2b shows the spatiotemporal mapping of the proton density in VO$_2$ from the simulation with $D = 150$ nm$^2$/s. Here, $x = 0$ represents the interface of the VO$_2$ contacted with the Pt electrodes. We divided the $2\mu$m-length VO$_2$ wire by 100 in the FDM calculation, thus the integral $i$ goes from 1 to 100 and the divided length ($\Delta x$) is 20 nm (further details in Section A of the Supplementary Information). The inset of Fig. 2b represents the proton diffusion behavior of a 4-$\mu$m-length VO$_2$ wire because the intercalation and diffusion behavior becomes symmetric at a 2-$\mu$m distance from the Pt electrodes. Through this analysis, we can clearly understand the transient behavior of proton diffusion in the VO$_2$ wires.

For conversion of the proton concentration in VO$_2$ to resistivity, a serial resistor model was used as shown in the lower illustration of Fig. 2a, which is represented by the following equation:

$$\rho(T) = \frac{1}{100} \sum_{i=1}^{100} \rho_i(T)$$  \hspace{1cm} (3)

The $\rho(T)$ can be simply defined as $(1 - n_{\text{HVO}_2})\rho_{\text{VO}_2} + n_{\text{HVO}_2}\rho_{\text{HVO}_2}(T)$, where $\rho_{\text{VO}_2}$ is the resistivity of metallic VO$_2$ and $\rho_{\text{HVO}_2}(T)$ is the temperature dependent resistivity of the insulating HVO$_2$.

The $\rho_{\text{HVO}_2}(T)$ was fixed at 0.0008 $\Omega$ cm between 300 K and 380 K because of its nearly constant value with reference to the VO$_2$ resistivity curve in Fig. 1c, while $\rho_{\text{HVO}_2}(T)$ varies with temperature. The experimental values of $\rho_{\text{HVO}_2}(T)$ were taken at the required temperature by referring to the temperature vs resistance curve of HVO$_2$ in Fig. 1b. Figure 2b shows the transient resistivity behavior with time for the 4-$\mu$m-, 6-$\mu$m-, and 10-$\mu$m-length VO$_2$ wires at 380 K. The red dot curves show the simulation results using Eqs. (1) to (3) with the appropriately selected diffusion constant for the proton that transforms the crystal structure from VO$_2$ to HVO$_2$, $D_{\text{HVO}_2} = 150$ nm$^2$/s at 380 K determined by the wire lengths of VO$_2$ with 4-$\mu$m, 6-$\mu$m, and 10-$\mu$m. The simulation curves could fit to the experimental curves well in their lengths. The diffusion value was compared with proton diffusion in the [001] direction of rutile-type TiO$_2$ without a structural transformation$^{25}$.

It is considered that the slower diffusion of constant of VO$_2$ [110] than that of TiO$_2$ [001] would be due to difference of two oxygen distance ($d_{\text{o-o}}$) in [001] and
[110] directions, respectively, because the diffusion constant of protons hopping to next oxygen sites is dependent on square length of $d_{o-o}$. The $d_{o-o}$ in TiO$_2$ [001] direction is approximately 1.48 Å$^{25}$, whereas the $d_{o-o}$ in VO$_2$ [110] and HVO$_2$ [110] are approximately 2.66 Å and 2.68 Å$^{13}$, respectively. Figure 2c shows the spatial mapping of the proton ratio using $D_{HVO_2} = 150$ nm$^2$/s in the 4-μm-, 6-μm-, and 10-μm-length VO$_2$ wires for 4 h after start from hydrogen intercalation. The occupancy of the protons was high at >80%/unit cell, even at the center of the 4-μm-length VO$_2$ wire, while the center of the 10-μm-length wire was still unoccupied by protons. The spatial density of HVO$_2$ clearly reflects the resistance behavior shown in Fig. 2b.
Discussion of the physical picture. Next, we estimated the activation energy ($E_{HVO2}$) for the structural transformation from VO$_2$ to HVO$_2$ using the experimental results of the 4-μm-length VO$_2$ wire and simulation fittings. Figure 3a–d show the time dependence of the resistivity behaviors in the 4-μm-length VO$_2$ wire at 320 K, 340 K, 360 K, and 380 K, respectively. (e) the red dots represent experimental $D_{HVO2}$ values in the VO$_2$ wire with structural transformation to HVO$_2$, estimated from the simulated fitting in Fig. 3a–d (the red dot lines). The red line is the fitting curve using Eq. (4). In comparison with the experimental $D_{HVO2}$, the proton diffusion constant of the parallel direction along the c axis of TiO$_2$, as a function of temperature in ref. 21 (black line). The inset shows the 1/T dependence of ln $D_{HVO2}$ for the Arrhenius plots.

Figure 3. Transient electronic transport behaviors of the 4-μm-length VO$_2$ microwire at a variety of temperatures. (a–d) Time dependence of the resistivity behaviors in the 4-μm-length VO$_2$ wire at 320 K, 340 K, 360 K and 380 K, respectively. (e) the red dots represent experimental $D_{HVO2}$ values in the VO$_2$ wire with structural transformation to HVO$_2$, estimated from the simulated fitting in Fig. 3a–d (the red dot lines). The red line is the fitting curve using Eq. (4). In comparison with the experimental $D_{HVO2}$, the proton diffusion constant of the parallel direction along the c axis of TiO$_2$, as a function of temperature in ref. 21 (black line). The inset shows the 1/T dependence of ln $D_{HVO2}$ for the Arrhenius plots.

\[
D(T) = D_0 \exp \left( -\frac{E_D}{k_B T} \right)
\]  

where $E_D$ is the diffusive activation energy and $D_0$ is the frequency factor.

Figure 3e shows temperature dependence of $D_{HVO2}$. The red dots represent the experimental $D_{HVO2}$ values in the VO$_2$ wire with structural transformation to HVO$_2$, estimated from the simulated red dot lines in Fig. 3a–d. The red line is the fitting curve using Eq. (4). Compared with our experimentally determined $D_{HVO2}$ values, the diffusion constant of protons in the direction parallel to the c axis of rutile-TiO$_2$ (black line) are reasonably similar. Considering the diffusion constant of protons in TiO$_2$, which is same crystal structure as VO$_2$, and the direct observation of proton diffusion in VO$_2$ by a microscope. In addition, at the section D in
Supplementary Information, resistance once insulating monoclinic-state of VO$_2$ at 290 K decreases in an insulating monoclinic-state of VO$_2$ at 290 K under a H$_2$(5%) + Ar(95%) gas atmosphere. This is due to carrier doping from OH group without crystal transformation, that is, carrier density increases keeping the tetragonal VO$_2$ structure. With further developing proton-intercalation, the heavy proton dopants promote transformation to the different crystal structure of insulating HVO$_2$$^{13}$. This transient response appears in Fig. S4. Thus, the origin of resistance changes in Figs. 2b, 3a–d and 4a can be more reasonably explained as proton diffusion in VO$_2$ than formation of contact resistance and/or small fractions having proton-puddles. The inset shows the $1/T$ dependence of ln$D_{HVO_2}$ for the Arrhenius plots. Figure 3e shows $1/T$ dependence of the $D_{HVO_2}$ values derived from the fitting curves using Eq. (4). The solid red line was obtained by the least-square method. From the slope, we determined that the diffusive activation energy for transformation from VO$_2$ to HVO$_2$ was 0.61 eV. For the diffusive activation energy for the reverse transformation from HVO$_2$ to VO$_2$, we estimated the diffusion coefficients ($D_{VO_2}(T)$). Figure 4a shows the transient normalized-resistance curves for the reverse HVO$_2$ to VO$_2$ transformation in a N$_2$ atmosphere at 300 K, 320 K, 340 K, 360 K, and 380 K, respectively. Simulation curves using the FDM calculations could be well fitted to the experimental curves by incorporating the temperature-dependent coverage of hydrogen adatoms on Pt surface$^{26}$ (Section B of the Supplementary Information provides further details). The $D_{VO_2}$ was 4600 nm$^2$/s at 300 K, 10000 nm$^2$/s at 320 K, 20000 nm$^2$/s at 340 K, 45000 nm$^2$/s at 360 K, and 90000 nm$^2$/s at 380 K, which were more than two orders higher than those of $D_{HVO_2}$. From the fitted $D_{VO_2}$ at various temperatures, the activation energy for the transformation from HVO$_2$ to VO$_2$ ($E_{VO_2}$) was determined to be 0.37 eV as obtained from the slope in Fig. 4b. Figure 4(c) shows the transformation energy between VO$_2$ and HVO$_2$ derived from the above data. VO$_2$ structure is more stable than that in HVO$_2$ structure.

**Discussion**

We clarified the physical parameters of heavily proton-intercalated VO$_2$ through investigation of proton diffusion. Single-crystal VO$_2$ thin films with a layer-by-layer growth were used to describe the crystal transformation energies from VO$_2$ to HVO$_2$ and from HVO$_2$ to VO$_2$. This was accomplished through investigation of the proton diffusion using the basic equations listed in Eq. (1) to Eq. (3). Data from in-plane poly-crystalline VO$_2$ thin films with grains on Al$_2$O$_3$ (0001) substrates$^{26}$ were not well-fitted to the ideal simulations using these equations. This was because a different crystal direction in-plane and grain boundaries disturb the ideal proton diffusion (Section C in Supplementary Information provides further details). It was found that the proton diffusion speed from HVO$_2$ to VO$_2$ was approximately two orders higher than that for VO$_2$ to HVO$_2$. The long-range micro-meter proton propagation, differences in the proton diffusion constants, and the asymmetry transformation energy between HVO$_2$ and VO$_2$ offer opportunity for the realization of novel iontronic applications and for energy devices, such as hydrogen storage.
Methods

Microwave preparation. Single crystal VO₂ thin films were epitaxially grown on TiO₂ (001) substrates using the pulsed laser deposition technique (ARF excimer laser, λ = 193 nm), with a substrate temperature of 420 °C, an oxygen partial pressure of 0.95 Pa, a laser repetition rate of 2 Hz, and with an energy fluency of 10 mJ/cm². A V₂O₅ pellet was used as the target. The deposition rate was ~0.3 nm/min. The thickness of the VO₂ thin films were fixed at ~10 nm. The films and Pt catalytic electrodes were patterned via photolithography. A 40-nm-thick Pt electrode was deposited on the patterned VO₂ microwires. The width (w) was fixed at 2 μm and the Pt electrode distance (d) was from 2μm to 10μm, as shown in the schematic in Fig. 1(a). The right image in Fig. 1a shows a VO₂ microwire with Pt electrodes as an example.

Measurements. The electronic properties of the films were measured via a two-probe method using a current-voltage source meter (2614B, Keithley Instruments) under H₂(5%) and N₂ gas atmospheres. The current flow direction was [110] in the rutile VO₂ thin films.

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Author contributions
K.M. fabricated the devices, conducted the measurements, analyzed the data, and wrote the manuscript. T.K. planned the research direction, supervised the experiment, analyzed the data, and the main manuscript text. All authors reviewed the manuscript.

Competing interests
The authors declare no competing interests.

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