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Electrical quadruple hysteresis in Pd-doped vanadium pentoxide nanowires due to water adsorption

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Abstract

Humidity-dependent current–voltage (I – V) characteristics of Pd-doped vanadium pentoxide nanowires (Pd-VONs) were investigated. Electrical quadruple hysteresis (QH) was observed and attributed to the large amount of water molecules adsorbed on the nanowires. Using QH in Pd-VONs, the reaction of water with PdO was interpreted as the water molecules are desorbed and then dissociated with increasing bias voltage. Owing to the dissociated H^+ and OH^- ions, PdO is reduced and oxidized. As a result, water molecules recombine as the bias voltage is decreased.

Keywords: Pd-doped vanadium pentoxide nanowire, electrical quadruple hysteresis, water adsorption

1. Introduction

The behavior of adsorbed water on metals has been the subject of numerous experimental studies. For example, it was shown that individual water molecules diffuse and cluster in immobile pentamers [1] and that they bond to a Pt surface through both oxygen and hydrogen atoms [2]. Also, many theoretical reports have been published regarding the behavior of water molecules on various metal surfaces [3, 4]. In the case of Ru(0001), the half-dissociation of the first water layer is reportedly favorable [5]. The barrier for dissociation of a chemisorbed H_2O monomer is 0.8 eV but that of a bilayer is 0.5 eV [6]. The dissociation barrier can be overcome by applying a bias voltage, as predicted by simulation of the changes in the structure of the water/Pd interface as a function of the applied voltage [7]. The dissociation of water on metals was confirmed by experiment, for example on Ru{0001} and Pt(111) surfaces using core-level photoelectron spectra [8] and temperature-programmed desorption [9], respectively. However, several studies demonstrated that water molecules remain intact rather than dissociate on various metal (110)

surfaces [3, 4], and that the dissociated and undissociated water molecules coexist [10].

These experimental and theoretical results indicate that the reactions of water molecules on a metal surface are poorly understood. These reactions change the electronic structure of the water/metal interface. If a corresponding electrical signal could be obtained from a metal particle-doped substrate, which is perturbed by an electrical potential in humid air, then the reactions of water on a metal could be deduced. In this work, we used nano-sized structures for this purpose because they can adsorb a larger amount of water molecules than bulk materials owing to their large surface area. Pd nanoparticle-doped vanadium pentoxide nanowires (Pd-VONs) were synthesized and the current–voltage (I – V) characteristics of the Pd-VONs were measured as a function of humidity. The results revealed electrical quadruple hysteresis (QH) due to the large amount of adsorbed water molecules. This electrical QH developed owing to the change in the depletion region originating from the contact between Pd nanoparticles and semiconducting vanadium pentoxide nanowires. From the analysis of the QH, we suggest that on Pd nanoparticles oxidized in air, the water

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molecules desorb, dissociate and recombine depending on the applied bias voltage.

2. Experimental details

2.1. Sample preparation

2.1.1 Pd-doped vanadium pentoxide nanowires. The Pd-VONs were prepared in accordance with the previously presented procedure of synthesizing Ag-doped vanadium pentoxide nanofibers [11]: 100 μ l (420 μ mol) of vanadium-oxytriisopropoxide (VOTIP, $\text{OV}(\text{OC}_3\text{H}_7)_3$, Aldrich) was dissolved in 80 ml of deionized water. With this solution, 15 mg (90 μ mol) of palladium acetate $(\text{CH}_3\text{COO})_2\text{Pd}$, Aldrich) was mixed in a glass vessel and stirred for 5 min at 70 °C. The resulting solution was then kept under ambient conditions.

2.1.2 Pd-sputtered vanadium pentoxide nanowires. V_2O_5 sols were prepared from 4 g of ammonium (meta)vanadate (Aldrich) and 0.4 g of acidic ion exchange resin (DOWEX 50WX8-100, Aldrich) in 80 ml of deionized water. The VONs were dried after alignment between two electrodes onto SiO_2/Si by dielectrophoresis. After drying, Pd was deposited on the dried VON network on SiO_2/Si using a magnetron sputtering system. The base pressure was 1×10^{-7} Torr, and the working pressure was 5 mTorr with Ar carrier gas.

2.2. I-V measurements

The measured device consisted of a highly *p*-doped SiO_2/Si substrate with Ti/Au electrodes spaced by 1 μ m; the electrodes had a height of 80/20 nm Ti/Au and a width of 1 μ m. Two microliters of a Pd-VON suspension was dropped on the device under the application of ac voltage (frequency = 13 MHz, peak to peak voltage of 5 V) between the electrodes for 5–20 s using a function generator (AFG3251, Tektronix). Then, nitrogen gas was blown on the sample for 1 min to dry the solvent. *I*–*V* measurements were conducted in a chamber filled with air. The suspended structure was accomplished with dielectrophoresis on a $\text{Si}_3\text{N}_x/\text{Si}$ substrate prepared using reactive ion etching. The electrical transport measurements were carried out with a semiconductor characterization system (4200-SCS, Keithley), an electrometer (6517A, Keithley), and a programmable voltage source (230, Keithley). The humidity-dependent *I*–*V* characteristics were collected using a humid chamber (TH-ME-065, JEIO Tech.) at 293 K. The samples were kept in a vacuum of $<10^{-2}$ Torr for 1 h before the *I*–*V* measurement at each humidity level.

2.3. Sample characteristics

The crystal structure of Pd-VONs was characterized with an x-ray diffractometer (XRD, Philips X'Pert) using graphite-monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Scanning electron microscopy (SEM) images of the suspended structure were obtained with an FEI Sirion 200 field-emission SEM (FESEM). Transmission electron

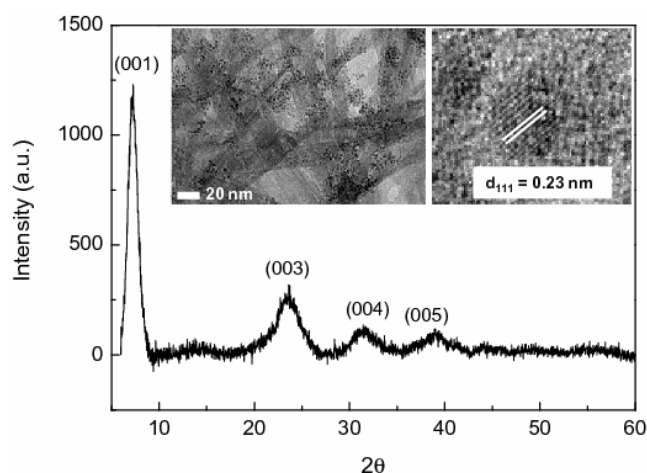


Figure 1. X-ray diffraction pattern of Pd-VONs revealing a layered structure that is similar to the XRD patterns of pure VONs. TEM images are shown in the inset. Pd ($d_{111} = 0.23 \text{ nm}$) nanoparticles are evenly distributed on the VONs.

microscopy (TEM) images were recorded using a 300 kV microscope (JEM 3010, JEOL Ltd) at a point resolution of 0.17 nm and pressure of $\sim 10^{-8}$ Torr.

3. Results and discussion

Figure 1 shows XRD pattern and TEM images of a Pd-VON. The structure of Pd-VONs is similar to that of pure VONs [12], suggesting that Pd doping did not significantly affect the layered structure of VONs. The high-resolution TEM image shows nanoparticles with a diameter of 2–3 nm attached to amorphous vanadium oxide nanowires of 10–20 nm width (inset of figure 1). Lattice fringes can be seen in the nanoparticles revealing the presence of nanocrystals. The measured interplanar spacing of 0.23 nm corresponds to that of the {111} planes of Pd (JCPDS data No. 87-0637, cubic symmetry, space group *Fm3m*).

Figure 2(a) shows the *I*–*V* characteristics of a Pd-VON network at 293 K in air, as measured after depositing the Pd-VON suspension onto Au electrodes by ac dielectrophoresis. A contact resistance of $\sim 13 \text{ M}\Omega$ was deduced from the comparison between the two-probe and four-probe measurements. When voltage was applied, QH arises in the *I*–*V* curve of the Pd-VON network but not for pristine VONs. QH was also observed in the four-probe measurements (inset of figure 2(a)). This implies that the QH is not affected by the contacts between the Pd-VON network and the Au electrodes. The current is suppressed at $V < 0.8 \text{ V}$, increases sharply between 0.8 and 1.5 V, and then steadily at 1.5–3.0 V. A hysteresis is observed upon lowering the applied voltage. The *I*–*V* characteristics are symmetric with respect to the origin. The QH disappears, and the current increases compared with that in air (figure 1(b)) if the sample is kept in a vacuum $<10^{-2}$ Torr. This result may indicate that the adsorption of some molecules from air or water molecules from the suspension causes both the QH and the decrease in the current in air. Therefore, *I*–*V* characteristics were measured in the presence of N_2 , O_2 , He, Ar and H_2

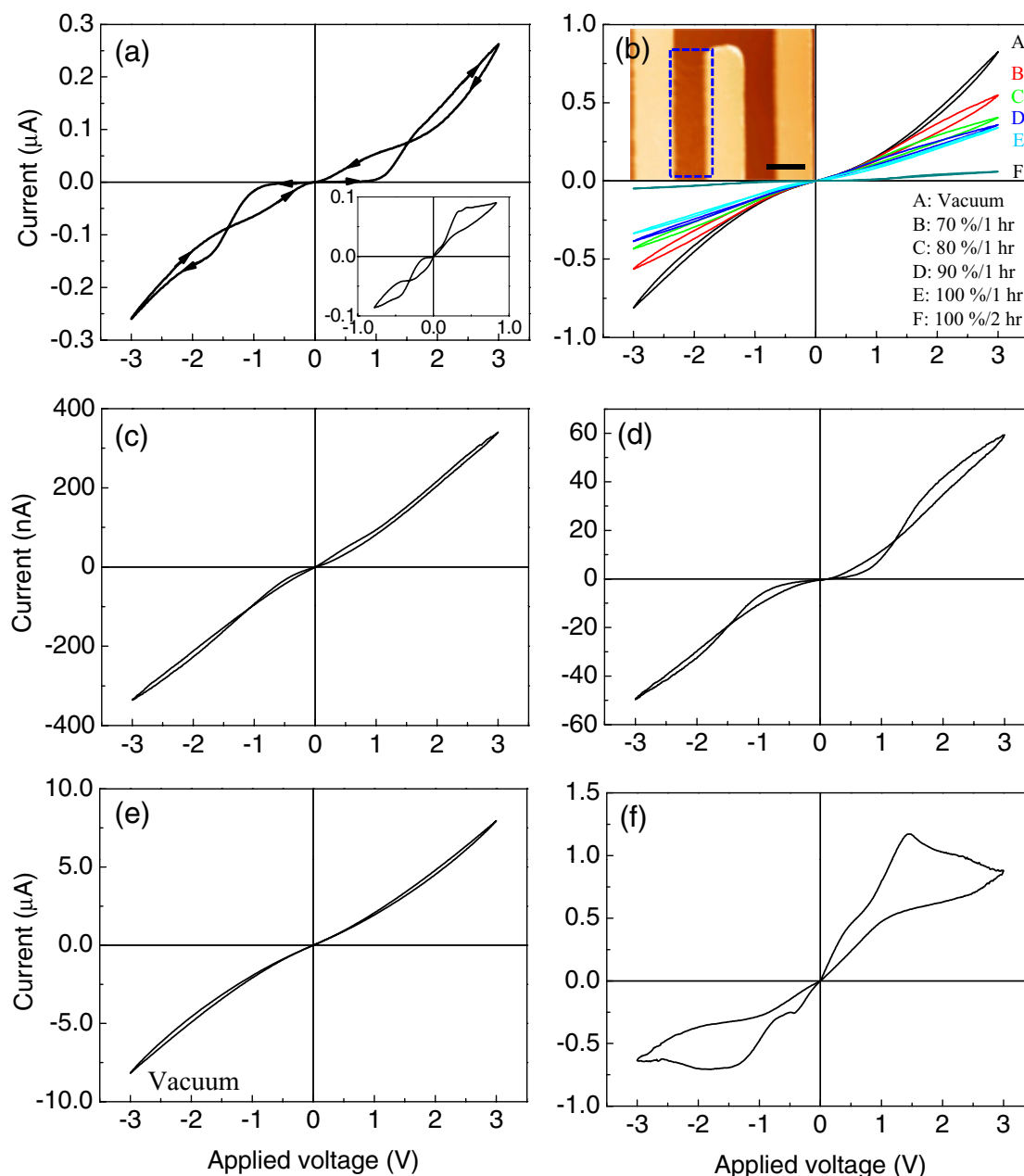


Figure 2. *I-V* characteristics of Pd-VONs. (a) QH occurs in the *I-V* curve; in a vacuum, this behavior disappears and the current increases. This indicates that certain elements in the air cause QH in Pd-VONs. The inset shows an *I-V* curve measured in the 4-probe configuration. (b) The Pd-VONs were kept for 1 or 2 h at each humidity level (A: vacuum; B: 70%/1 h; C: 80%/1 h; D: 90%/1 h; E: 100%/1 h; and F: 100%/2 h). As the humidity increased, the current decreased monotonically. However, the current decreased sharply at 100% humidity for 2 h. The inset (dashed box) shows an atomic force microscopy image of the Pd-VON network deposited by dielectrophoresis. The scale bar is 1 μm . (c) The sign of the QH is seen in a negative bias region at 100% humidity (1 h). (d) QH is clearly seen after exposure to humid air (100%, 2 h). (e) In the case of pristine VONs, weak hysteresis was observed in a vacuum. (f) Even under a humid condition (100%, 2 h), the QH does not occur in the pure VONs. The voltage sweep rate was 10 mV s^{-1} in all measurements.

gases [13]. Although the variation of the current is quite small, even at 10 atm (except for H_2 adsorption), a pressure increase gives rise to the current for all the tested gases except oxygen. This behavior is similar to the pressure-dependent current variation in pure VONs. No QH was observed with these gases [13].

Another adsorbant that should be considered is water from the Pd-VON suspension, and thus the humidity-dependent *I-V* characteristics were measured

(figures 2(b)–(d)). The current decreases as the humidity increases, and no QH was observed, even after exposure to air at 90% humidity for 1 h. However, QH developed after exposure at 100% for 1 h (figure 2(c)) and was clearly observed at 100% for 2 h (figure 2(d)). This proves that the presence of a large number of water molecules is required for QH. The QH could also be induced by exposure to a humid condition after drying the sample. In order to confirm whether QH develops in pristine VONs, their *I-V* characteristics

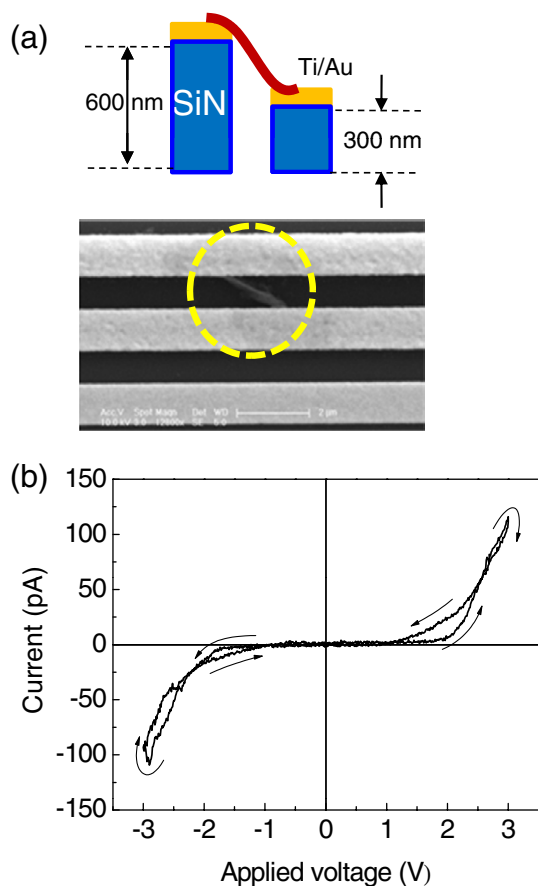


Figure 3. (a) An illustration of a suspended Pd-VON bundle and an SEM image revealing that the diameter of the bundle is close to 150 nm. (b) The I - V curve of the suspended Pd-VON bundle does show QH, indicating that the bound water on SiO_2 does not significantly affect the QH.

were measured in vacuum and in air at 100% humidity (figures 2(e) and (f), respectively). Under humid conditions, the current of the pristine VONs was significantly suppressed, the same as the current of the Pd-VONs; however, no QH was observed for the pristine VONs. Figure 2(f) shows the I - V characteristics of the pristine VONs under humid conditions (100%, 2 h).

It is unclear, however, whether the QH originates from the water bound on the SiO_2 surface [14] or coming from the Pd-VON conduction channels. Therefore, a suspended structure was created and its I - V characteristics were measured as shown in figure 3(a). The QH was generally similar in the suspended and non-suspended structures, although the details were not identical (figure 3(b)).

To check the effect of other synthesis parameters on the QH, Pd was decorated onto VONs between two Au electrodes using dc sputtering ($^{\text{S}}\text{Pd}$ -VON). The SEM images of the $^{\text{S}}\text{Pd}$ -VON network between two Au electrodes and Pd clusters are shown in figures 4(a) and (b), respectively. The image of $^{\text{S}}\text{Pd}$ -VON indicates that Pd particles are well deposited on the VON network. Figures 4(c) and (d) show the I - V curves in vacuum and humid environment, respectively. At 100% humidity, QH developed in $^{\text{S}}\text{Pd}$ -VONs, indicating that other elements that are added during the synthesis of the

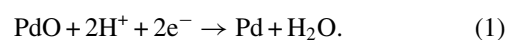
Pd-VONs, e.g. the amount of palladium acetate, do not affect the development of QH in the Pd-VONs.

Figure 5(a) presents a simplified model of the I - V characteristics at positive bias that qualitatively explains the QH. To develop the model, we first conducted an x-ray photoelectron spectroscopy study that showed that Pd 3d spectra correspond to the $3d_{5/2}$ and $3d_{3/2}$ levels of PdO [13]. This finding indicates that Pd was oxidized as soon as it was exposed to air. In addition, in the case of nanocontact between the nanoparticles and a semiconductor nanowire, the charge redistribution at the interface generates a depletion region in the semiconducting nanowires [15–17]. Therefore, the origin of the QH was attributed to i) possible reactions of water molecules on PdO, where PdO acts as a gate changing the depletion region in the VONs and ii) the reduction and oxidation of PdO due to the reactions of the water molecules.

Water molecules on the top site of a metal are most stable compared with those on the other sites, e.g. the bridge or a hollow site. The bonding between a metal and oxygen of water molecules induces a large charge transfer from the oxygen to the metal [3]. This charge transfer from oxygen to PdO causes Coulomb repulsion between the electrons in PdO and the n -type carriers in the VON. As a result, the depletion region is enhanced in the VON (figure 5(I)) and the current is suppressed (region I in figure 5(a)). The large number of water molecules plays a role in the occurrence of QH, as shown in figure 1. This implies that the dissociation of water is related to the QH, as the dissociation barrier decreases as the water quantity increases. For example, the dissociation barriers are 0.94 eV for a single water molecule and 0.57 eV for 1 monolayer of water on Cu [3], as Pd(111) is the borderline for a dissociative water bilayer or cluster adsorption [18], or because O–H bond cleavage can occur owing to the high hydrogen affinity at the metal surface [2]. However, as only 1/4 of the water molecules on Cu [3] and 9% of the water on Pt(111) [19] are reportedly dissociated, the effect of the dissociative water will be negligible compared with the effect of water molecules in this low bias voltage region.

In region II, the current increases abruptly. As the bias voltage increases, the number of water molecules on the PdO decreases because the desorption energy of water on metal is usually smaller than the dissociation energy; this results in a narrower depletion region (figure 5(II)). In addition, the dissociation occurs much more readily compared with that in region I owing to the bias voltage [7]. It most likely causes the charge to be transferred from the metal to the adsorbates, as described in a recent theoretical study [3].

The dissociation of water molecules to H^+ and OH^- becomes stronger in region III than in region II. Consequently, the reduction of PdO on the VONs begins as



The dissociation narrows the depletion region in the VON. In contrast, the recombination of the water molecules broadens the depletion region. The competition between the dissociation and recombination of H_2O results in a monotonic

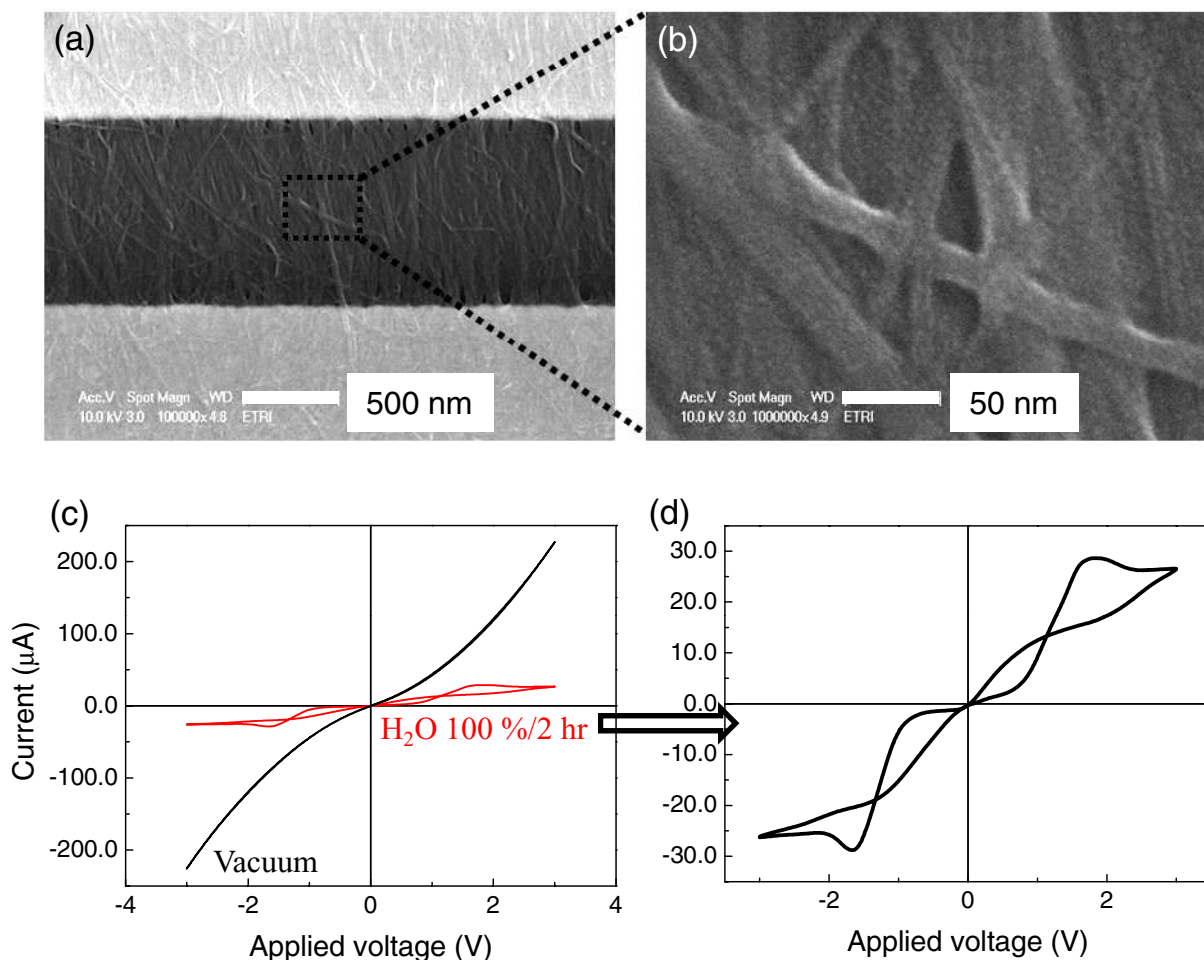
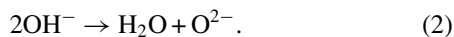


Figure 4. SEM images of (a) Pd-sputtered VONs. (b) Pd clusters are displayed in the magnified image. (c) *I*–*V* curves in vacuum and humid environment. (d) The QH in *I*–*V* characteristics is also seen in Pd-sputtered VONs.

increase in the current compared with that in region II (figure 5(III)).

In region IV, where the first hysteresis arises, the reduction becomes dominant. This is ascribed to the conversion of PdO to Pd and charge transfer from H₂O to Pd. Moreover, the reaction of hydroxyl ions also produces water molecules (reaction (2)). As a result, the current drops sharply compared with that in region III (figure 5(IV)).



In region V (figure 5(V)), the Pd produced in reaction (1) is oxidized owing to the O²⁻ in reaction (2) (reaction (3)). This process starts regenerating PdO. In this region, numerous water molecules are recombined relative to region II as a consequence of reactions (1) and (2); therefore, a significant current suppression is expected. However, because Pd and PdO coexist in the system, the current decreases slowly compared with that in region II. This is due to the difference in the work functions between Pd and PdO. The electrons of Pd are easily transferred to the VON compared with those of PdO because the work function of Pd (4.95 eV) is smaller than that of PdO (5.4 eV) [20, 21].



Finally, as water molecules recombined on PdO are dominant in the system and because the bias voltage decreases, the current drops sharply relative to that observed in region V, as shown in figure 5(VI) (region VI).

4. Conclusions

Pd-VONs were synthesized and their *I*–*V* characteristics were measured in humid air. Electrical QH was observed in Pd-VONs in the presence of a large number of water molecules. To avoid the effects of SiO₂-surface bound molecules and of other elements added in the synthesis process, *I*–*V* characteristics were measured in suspended Pd-VON and ⁵Pd-VON networks, and the QH was observed in both samples. The possible reactions of water molecules on PdO are suggested from the variation of current in Pd-VONs in humid air as a function of bias voltage. The water molecules are desorbed and then dissociated with the increase in the bias voltage. The dissociated H⁺ and OH⁻ ions cause reduction of PdO (PdO + 2H⁺ + 2e⁻ → Pd + H₂O) followed by recombination of water molecules (2OH⁻ → H₂O + O²⁻), and the latter process oxidizes Pd (Pd + O²⁻ → PdO). Even though these reactions of water molecules on a metal were

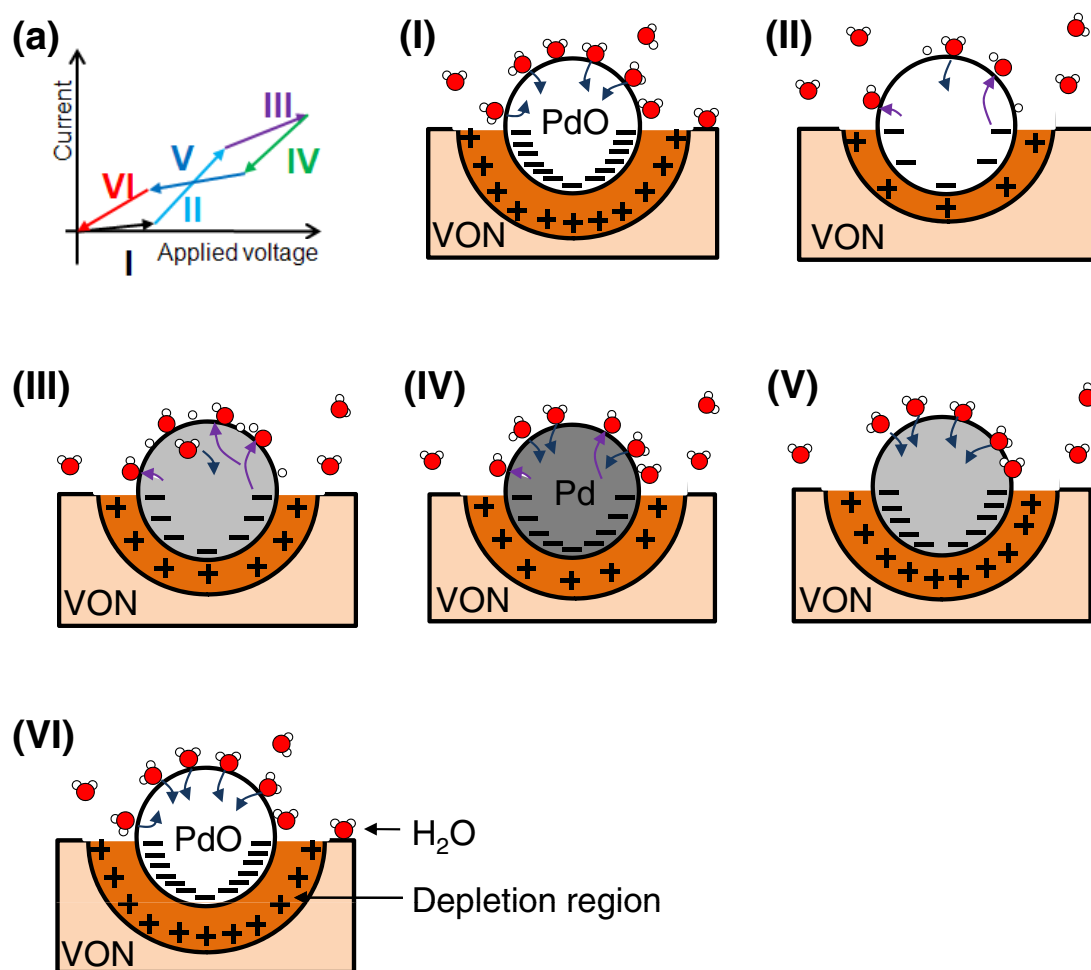


Figure 5. A model of the quadruple hysteresis. (a) To describe the variation of the current in Pd-VONs, the I - V characteristics are depicted in the positive bias regions (I–VI). The hydrogen and oxygen molecules of water are represented by the small white and large red circles, respectively. The depletion region, VON, PdO and Pd are colored in orange, light brown, gray and dark green, respectively. The arrows indicate the direction of the electron transfer.

deduced using an indirect method, they provide a progressive step to understanding the behavior of water on a metal surface.

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