

Reversible Gas-Solid Reaction in an Electronically-Stimulated Palladium Nanogap

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Supporting Information

SI 1. Preparation, *in-situ* ETEM and electric measurement of palladium nanogaps

A needle-shaped palladium electrode with a sharp tip was prepared by polishing a palladium wire (99.95% pure and 0.2 mm in diameter) electrochemically in a solution comprising HCl aq. (35–37 mass%) and ethanol as an electrolyte (HCl aq.: ethanol = 2:3 in volume) at room temperature. A DC voltage of 8.0 V was applied between a palladium wire and a gold ring as an anode.^{1,2} To smooth the surface of the tip, it was etched in a low HCl aq. concentration solution (HCl aq.: ethanol = 1: 9 in volume). After each process, palladium tips were rinsed with distilled water and ethanol and were heated for 5 minutes at 150 °C. Because the surface of palladium tips after electrochemical polishing and post-treatment was covered with hydrocarbon contamination, the palladium tips were further polished using Ar ion milling (Gatan, Inc. Precision Ion Polishing System 2).

A pair of palladium electrodes with the sharp and clean tip was set in an STM-TEM specimen holder.³ A palladium electrode was fixed to the holder and the other was mounted on a stage with piezo elements in the holder. After the palladium electrodes set in the holder were transferred to ETEM apparatus (FEI Titan ETEM G2)⁴, the electrodes were electrically connected to a measure source unit (KEYSIGHT B2902A) to apply the biasing DC voltage in the range 0 to ± 10 V. Residual contamination on the surfaces of the tips was further eliminated by electron-beam irradiation in O₂ (100 Pa) in the ETEM apparatus with high electron current density (400 A/cm²) for 120 s. The surface of the tips was slightly oxidized by this process. The oxide on the surface was reduced in H₂ (100 Pa) for 2 hours. After the oxide was reduced, the distance between the tips was reduced to a few nanometers using a piezo element. The palladium nanogaps were then characterized using ETEM and the measurement of the electric current between the tips or across the palladium nanogap at room temperature in a vacuum (1×10^{-4} Pa), H₂ (100 Pa), O₂ (100 Pa) and N₂ (0.01 Pa ~ 100 Pa). All environments were controlled using Residual Gas Analyzer (RGA). The hydrogen gas was composed of H₂ (97.285 %), N₂ (0.139 %), O₂ (0.595 %), Ar (0.047%), and H₂O (1.663 %). The oxygen gas was composed of O₂ (99.550 %), N₂ (0.055 %), H₂ (0.006 %), Ar (0.014%), and H₂O (0.342 %). The nitrogen gas was composed of N₂ (99.967 %), O₂ (0.004 %), H₂ (0.013 %), Ar (0.002%), and H₂O (0.013 %). The accuracy of electric current measurement was 0.1 nA. The distance between the tips could be varied using the piezo elements and was measured directly by ETEM. The ETEM apparatus is equipped with a corrector of the spherical aberration of the objective lens and is operated at 300 kV. Electron current density on a specimen in ETEM observation, Φ was estimated to be 100 A/cm² or otherwise noted in text. ETEM images were recorded using a CCD camera with a time resolution of 0.5 s.

TEM image simulation was conducted using MACTEMPAS software package (Total Resolutions, Berkeley, CA, USA). The parameters for simulation were accelerating voltage of 300 kV, spherical aberration coefficient of 1 μm for the objective lens, chromatic aberration coefficient of 1.4 mm for the objective lens and objective aperture radius of 10 nm⁻¹. Halfwidth of mechanical vibration in the lateral and longitudinal plane were 0.1 nm and 0.05 nm, respectively, because mechanical vibration in the lateral plane was larger than that in the longitudinal plane in our experiment.

SI 2. Measurement of tunneling barrier height in vacuum

To evaluate the tip surface of palladium electrodes electrically, the tunneling barrier height of a palladium nanogap was measured in a vacuum using ETEM apparatus (Figure S1). The tunneling current was measured after the cleaning process of the tip surface as described in SI 1. Figure S1 (a) and (b) shows typical results of *in-situ* TEM observation of an electrically-biased palladium nanogap in vacuum synchronized with the measurement of a tunneling current. Tunneling current is represented by:⁵

$$I \propto \exp(-1.025d\sqrt{\varphi}),$$

where I , d and φ represent tunneling current in nA, gap distance in Å and tunneling barrier height in eV, respectively. In this study, d was directly measured from TEM images. Figure S1 (c) summarizes I as a function of d for $V = 1.0$ and 4.0 V in vacuum and measured $V = 1.0$ V in N_2 (100 Pa). The tunneling barrier height in a vacuum was estimated to be 4.8 ± 0.4 eV for 1.0 V and 4.8 ± 1.1 eV for 4.0 V; these values are similar to the work function of palladium reported in the literature.⁶ For higher biasing voltages over 7.0 V, the work function was apparently reduced. Electrons can also be emitted from an area around the tip. A tunneling current is slightly reduced from that in a vacuum by introducing nitrogen gas into the palladium nanogap.

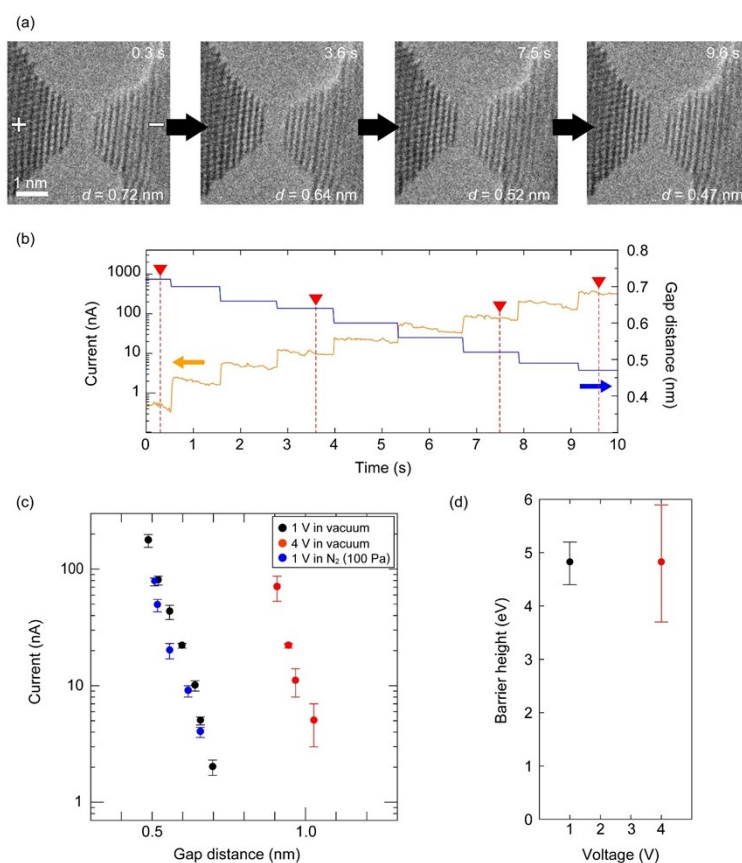


Figure S1. (a) and (b) *In-situ* TEM observation of an electrically-biased palladium nanogap with the simultaneous measurement of tunneling current, I for an estimation of the tunneling barrier height of a palladium nanogap in vacuum (10^{-4} Pa). The biasing voltage, V , is 1.0 V. Lapse time and measured gap distance, d , is indicated in the images. TEM images are taken at the time indicated by red triangles with red broken lines. (c) I is summarized as a function of d for $V = 1.0$ V and 4.0 V in vacuum and $V = 1.0$ V in N_2 (100 Pa). (d) The tunneling barrier height in a vacuum is estimated from (c).

SI.3 Reproducibility and reversibility of the gas-solid reaction

To confirm the reproducibility and reversibility of the gas-solid reaction, we repeated ETEM observations on several sets of palladium tips. Figure S2 summarizes typical ETEM observations on two different sets of palladium tips. Movie 1 shows the reversible reaction, synchronized with the measurement of an electric current in another set of Pd tips. The images in (c) in Figure 1 are taken from Movie S1.

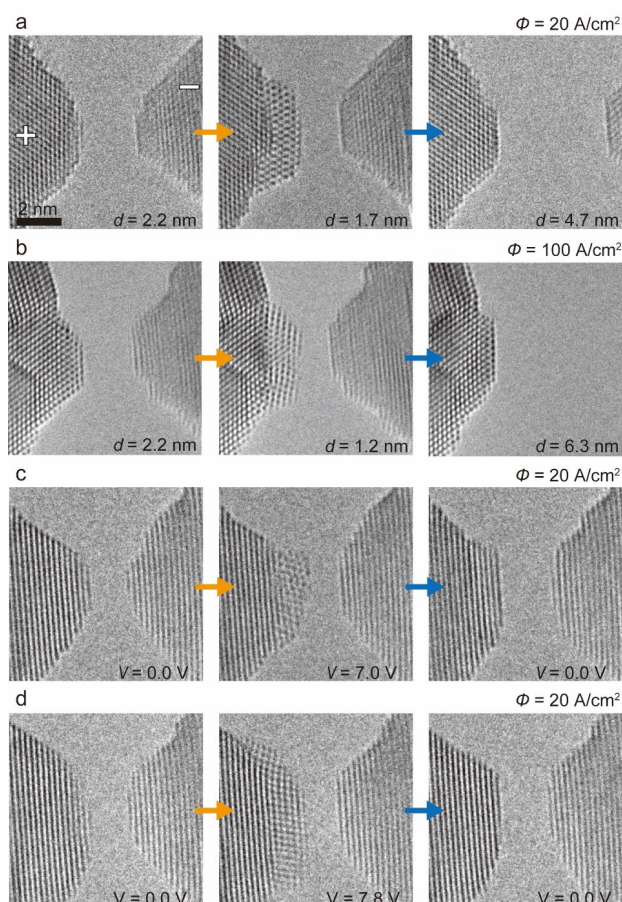


Figure S2. Reproducibility of the reversible gas-solid reaction on the tip surface of the positive electrode in an electrically-biased palladium nanogap with nitrogen gas. The magnitude of an electric field in a nanogap was increased (orange arrows) and decreased (blue arrows) by varying the gap distance, d , while keeping biasing voltage, V , constant at 10.0 V in (a) and (b) and by varying V while keeping d constant at 1.4 nm in (c) and (d). The set of tips in (a) and (b) is different from that in (c) and (d). Nitrogen pressure, P , was 100 Pa. The incident electron beam was parallel to the [010] direction in (a) and (c) and to the [111] direction in (b) and (d) in the PdN compound with cooperite structure. Electron current density during ETEM observation, Φ is indicated in (a) to (d).

SI. 4 Pd nanogaps in vacuum, H₂, O₂ and N₂

We checked the tip surface of palladium electrodes in a vacuum, hydrogen gas (100 Pa), oxygen gas (100 Pa), and nitrogen gas (100Pa), as summarized in Figure S3. In a vacuum (Figure 3(a)), palladium atoms on the tip surfaces of both electrodes are rarely sputtered out independent of the magnitude of an applied electric field in the nanogap, which was below 8.8 V/nm in this study. However, when we introduce hydrogen and oxygen into the nanogap, palladium atoms are

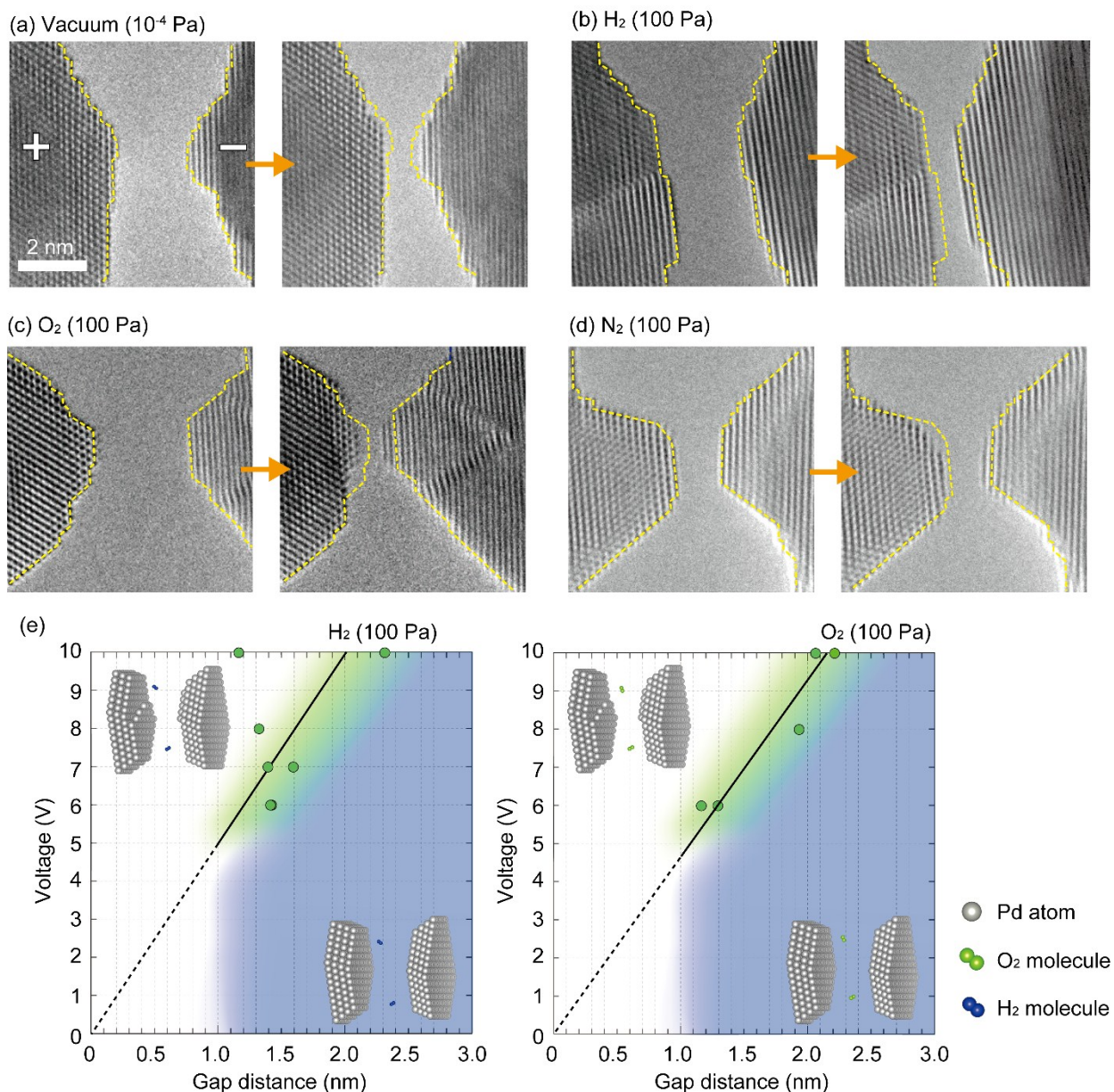


Figure S3. Evaporation and deposition of Pd atoms in an electrically-biased Pd nanogap in gases. (a) In a vacuum as reference, (b) in hydrogen gas (100 Pa), (c) in oxygen gas and (d) in nitrogen gas (100 Pa). The magnitude of an electric field was increased (orange arrow) by decreasing gap distance, d , while keeping biasing voltage, V , constant at 7.0 V. Broken yellow curves in the images indicate the outline of the tips before decreasing d . In a vacuum in (a), palladium atoms on both the positive and the negative electrodes are gradually removed via knock-on damage by high-energy electron (300 keV) irradiation regardless of V . In hydrogen gas and oxygen gas in (b) and (c), palladium atoms are preferentially evaporated from the positive electrode tip and deposited on the negative electrode tip. Condition for evaporation and deposition in hydrogen and oxygen is summarized in (e). Face-centered cubic (fcc) palladium on the tip surfaces of both electrodes remains entirely stable in the blue region, while evaporation and deposition are induced and marked by green circles. The threshold magnitude of an electric field, V/d , for the evaporation and deposition in hydrogen and oxygen may be roughly estimated to be 5.2 ± 0.5 V/nm and 4.7 ± 0.1 V/nm, respectively. Gap distances smaller than approximately 1 nm were difficult to explore experimentally. In nitrogen gas (100 Pa), the evaporation and deposition are only observable as is shown in (d) before the drastic gas-solid reaction occurs.

evaporated from the tip surface of the positive electrode and deposited on that of the negative electrode (Figure S3(b) and (c)). By evaporation and deposition of palladium atoms, the tips are reshaped significantly while keeping the crystal structure of the surface and interior of the tips face-centered cubic. No stable compound structures could be identified on the tip by ETEM because the estimated lattice expansion caused by hydrogen atom penetration at 100Pa is less than 3%.⁷ Electron energy loss spectroscopy could not detect either such a small amount of hydrogen atoms in Pd⁸. In nitrogen gas, as is described in text, the drastic gas-solid reaction creates the PdN compound on the tip surface of the positive electrode. Before the drastic reaction, the evaporation and deposition of Pd atoms was observed (Figure S3(d)).

SI. 5 Effect of electron irradiation on the gas-solid reaction

To examine the effect of electron irradiation, the electrode surfaces are observed in nitrogen gas with different electron current densities, Φ from 100 A/cm² to 1 A/cm² (Figure S4). Even at a lower electron current density (1 A/cm²), we could clearly confirm the creation of the PdN compound on the tip surface of the positive electrode. The size of the PdN compound was independent on a range of electron current densities from 100 A/cm² to 1 A/cm². The threshold electric field to create the PdN compound is in the same order of magnitude, i.e. 4 to 5 V/nm in the range of electron current density. We blanked an electron beam to detect the sudden increase in electric current across the palladium nanogap by increasing a biasing voltage without high-energy electron irradiation. However, the sudden increase was not reproduced without high-energy electron irradiation. Although we could not rule out the possibility of the gas–solid reaction without electron irradiation, the reaction is most likely induced by electronic excitations in the palladium nanogap with nitrogen gas, involving high-energy electrons and associated secondary electrons that are emitted from the electrode surfaces by the irradiation of high-energy electrons. Because the energy dissipation process of high-energy electrons in materials for electronic and atomic interactions is extremely difficult to handle quantitatively, further discussion on the mechanism for the gas-solid reaction is beyond the scope of this experimental study.

The evaporation and deposition of palladium atoms in gases (Figure S3(d)) is likely induced by the activation of gases and surface palladium atoms. It is known that gas molecules can be ionized in a strong electric field. The threshold magnitude of an electric field for ionizing hydrogen molecules and nitrogen molecules are 18.8 V/nm⁹ and 16.5 V/nm,⁹ respectively. The magnitudes are larger than those needed to evaporate and deposit gases in this study. Therefore, ionization, caused only by an electric field is ruled out in this study. To evaluate the ionization of gas molecules by energetic electrons, we look to the literature. The collision cross-section for the ionization of gas molecules could be measured only for low energy electrons: the cross-section for the ionization of a nitrogen molecules by electrons of 600 eV is estimated to be 0.01 nm¹¹. Therefore, the collision cross-section for the ionization of gas molecules is significantly small for high energy electrons (300 keV) in this study. It is also known that atoms on a surface are field evaporated under a high electric field.⁹ For palladium, the threshold electric field is estimated to be approximately 30 V/nm in a vacuum.¹⁰ Accordingly, in our experiment, no field evaporation occurs in a vacuum (up to 8.8 eV/nm). Nevertheless, in hydrogen gas and nitrogen gas, the evaporation and subsequent deposition of palladium atoms are induced far below the threshold magnitude of an electric field in a vacuum. Though the correlation of the evaporation and subsequent deposition with the gas-solid reaction is interesting, further discussion is beyond the scope of this experimental study.

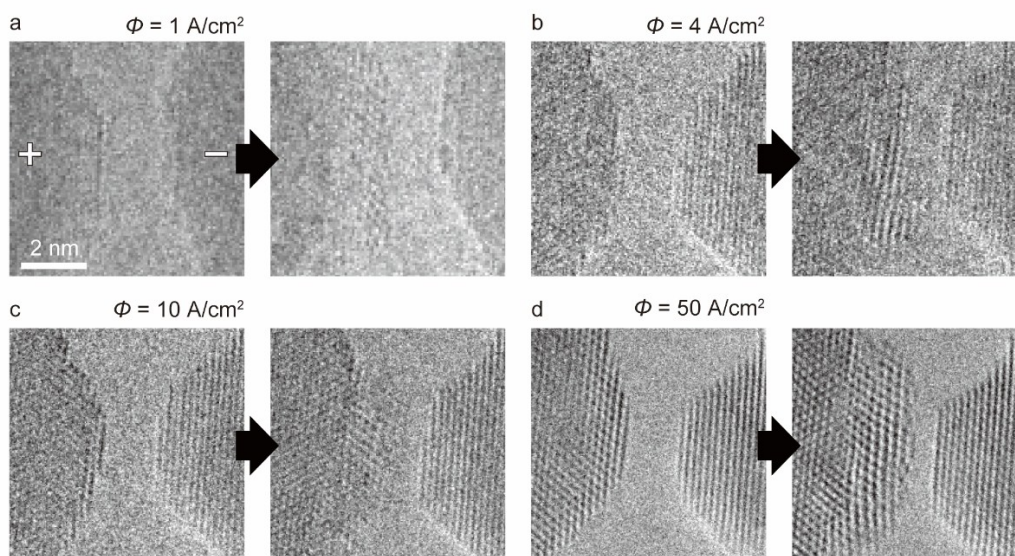


Figure S4. Dependence of electron current density on the gas-solid reaction. Electron current densities, Φ were 1 A/cm² (a), 4 A/cm² (b), 10 A/cm² (c) and 50 A/cm² (d). Nitrogen gas pressure, P , was kept constant at 100 Pa and biasing voltage, V , was kept constant at 7.0 V. The PdN compound is created independent of the magnitude of electron current density.

Caption for Movie

Movie 1. *In-situ* ETEM observation of a reversible phase transition in an electrically-biased palladium nanogap. The images in Figure 1 are taken from Movie 1.

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