Enhanced hydrogen permeability of hafnium nitride nanocrystalline membranes by interfacial hydridic conduction

Chiharu Kura,[1] Sho Fujimoto,[2] Yuji Kunisada,[3] Damian Kowalski,[3] Etsushi Tsuji,[4] Chunyu Zhu,[3] Hiroki Habazaki,[3] and Yoshitaka Aoki[3,5]*

1. Graduate School of Chemical Sciences and Engineering, Hokkaido University, N13W8 Kita-ku, Sapporo, 060-8628 Japan.

2. Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto, 611-0011 Japan.

3. Faculty of Engineering, Hokkaido University, N13W8 Kita-ku, Sapporo, 060-8628 Japan.

4. Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Tottori 680-8552, Japan.

5. JST-PRESTO, 4-1-8 Honcho, Kawaguchi 332-0012, Japan.

*Corresponding author

Yoshitaka Aoki

Associate Prof.

Faculty of Engineering, Hokkaido University, N13W8 Kita-ku, Sapporo, 060-8628 Japan.

Tel: +81-11-706-6752; e-mail: y-aoki@eng.hokudai.ac.jp

Supplementary figures

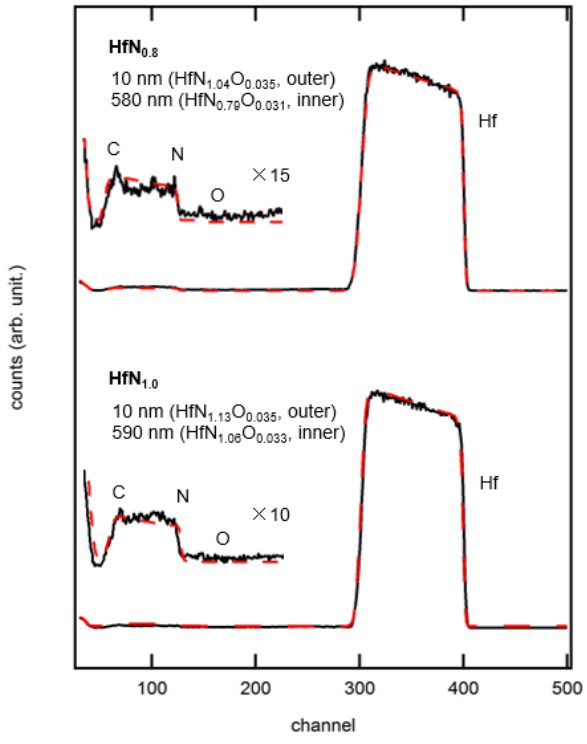

Fig. S1 RBS depth profiles of $HfN_{0.8}$ and $HfN_{1.0}$ films (600 nm) prepared on glassy carbon substrates. Black lines are the observed and red dots the simulated. Their corresponding chemical composition is $HfN_{0.79}O_{0.031}$ ($HfN_{0.8}$) and $HfN_{1.06}O_{0.033}$ ($HfN_{1.0}$), respectively. The surfaces of both films are oxidized by air, forming 10 nm-thick outerlayer.

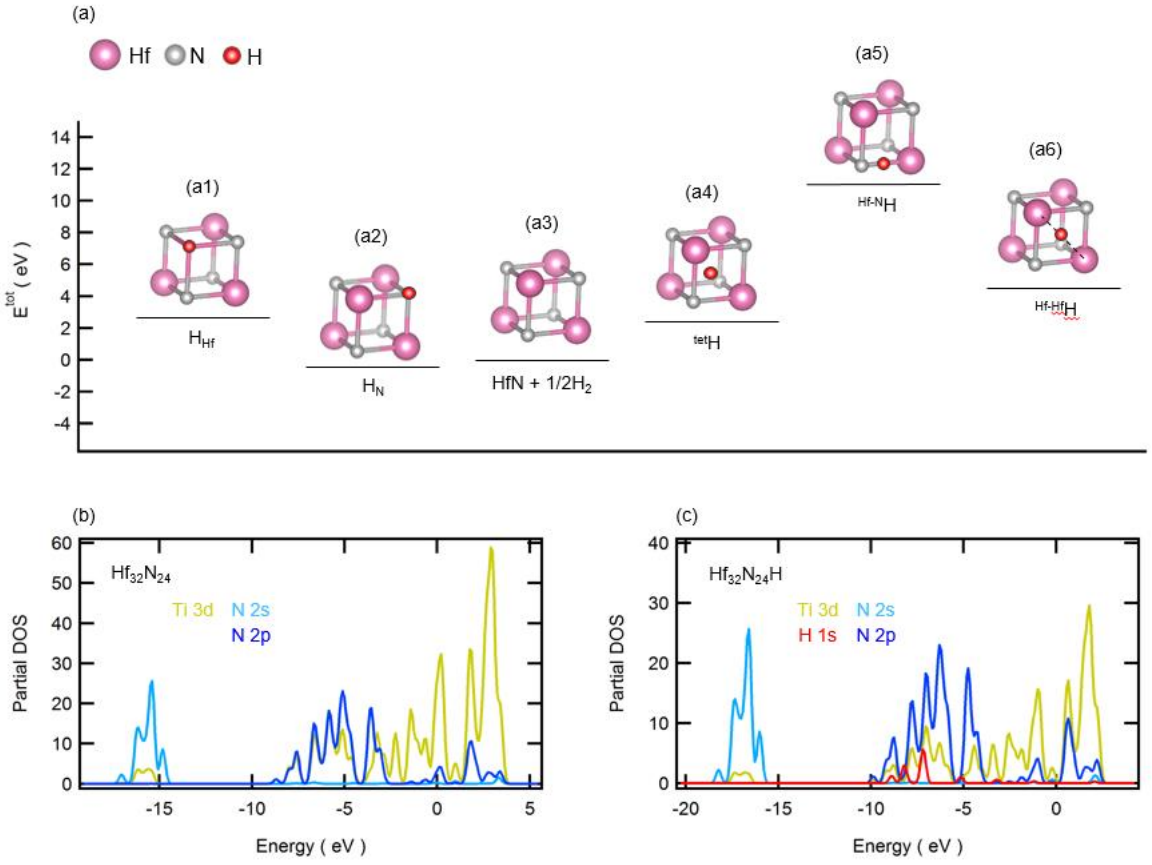

Fig. S2 (a) The DFT energies calculated for 2×2×2 supercells of various hydrogen defect models. (a3) shows the total energies of the system comprising stoichiometric HfN phase ($Hf_{32}N_{32}$) and 1/2 H_2 gas. (a1) $Hf_{31}N_{32}(H_{Hf})$: H defect occupying a Hf vacancy of Hf-deficient $Hf_{31/32}N$ phase. (a2) $Hf_{32}N_{24}(H_N)$: H defect occupying a N vacancy of N-deficient $HfN_{24/32}$ phase. (a4, a5, a6) $Hf_{32}N_{32}H_1$: HfN phase with an H interstitial at (a4) tetrahedral site of fcc Hf sublattice (^{tet}H), (a5) center of the closest Hf-N bond ($^{Hf\text{-}N}H$) and (a6) center of the closest Hf-Hf bond ($^{Hf\text{-}Hf}H$). (b), (c) Partial DOS of $Hf_{32}N_{24}$ and $Hf_{32}N_{24}H$. H 1*s* state is offset by ×2.

Method to determine the p_{H2} at TiN_x/Al_2O_3 support interface

When hydrogen permeates through TiN_x/Al_2O_3 support structure, the resulting pressure profiles depend on the properties of each layer. At steady state, hydrogen flux J_{H2} is equivalent to one of Al_2O_3 support, and the hydrogen partial pressure at entrance and exit sides are defined as p_{H2}' and p_{H2}''', respectively. Here, p_{H2}' and p_{H2}''' are known, the pressure p_{H2}'' at interface between TiN_x and porous alumina can be determined with the flux calibration curve of porous supports by the following way.

The hydrogen permeance of Al_2O_3 support, φ_2, has been given by equation 1,[S1]

$$\varphi_2 = \frac{J_{H2}}{(p_{H2}'' - p_{H2}''')} = \alpha + \beta \times \frac{(p_{H2}'' + p_{H2}''')}{2} \quad (1)$$

where $(p_{H2}''+ p_{H2}''')/2$ gives an 'average' pressure of Al_2O_3 support. Accordingly, the plots of φ_2 vs. $(p_{H2}''+ p_{H2}''')/2$ show a clear linear relationship.[S2] Therefore, p_{H2}'' can be determined by reading the average pressure corresponding to the J_{H2} from the calibration curve. Hence, p_{H2}'' is determined by

$$p_{H2}'' = \frac{-\alpha + \sqrt{\alpha^2 + 2\alpha\beta p_{H2}''' + \beta^2 p_{H2}'''^2 + 2\beta J_2}}{\beta} \quad (2)$$

Reference

(S1) N. Itoh, T. H. Wu and K. Haraya, *J. Membr. Sci*. 1999, **99**, 175-183.

(S2) C. Kura, Y. Kunisada, E. Tsuji, C. Zhu, H. Habazaki, M. P. Müller, R. A. de Souza and Y. Aoki, *Nat. Energy*, 2017, **2**, 786-794.