## Electronic Supplementary Information (ESI) High resistance of superconducting TiN thin films against environmental attacks

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## I. EXPERIMENTAL



FIG. S1. The photographs and schematic crystal structures of (a) single-crystalline TiN (111) films and (b) polycrystalline TiN films. Both of them were immersed in HCl for 4 days. The polycrystalline TiN film has been destroyed, whereas the single-crystalline TiN film can survive.



FIG. S2. (a) The schematic of the TiN crystal structure. The photographs of (b) (111)-oriented single-crystalline TiN films on  $Al_2O_3$  (0001) substrates and (c) (001)-oriented single-crystalline TiN films on MgO (001) substrates immersed in the HCl solution after 3 days. The (001)-oriented TiN films have been destroyed, whereas the (111)-oriented TiN films retained the bright golden color.



FIG. S3. Temperature-dependent I-V curves of (a) pristine TiN films, (b) TiN films immersed in HCl for 6 days, and (c) TiN films immersed in KOH for 9 days. The critical current densities are  $J_c(5.4 \text{ K}) \approx 21 \text{ kA/cm}^2$  for pristine TiN films,  $J_c(5.4 \text{ K}) \approx 21 \text{ kA/cm}^2$  for TiN films immersed in HCl for 6 days, and  $J_c(5.3 \text{ K}) \approx 12 \text{ kA/cm}^2$  for TiN films immersed in KOH for 9 days (the thickness is around 50 nm).



FIG. S4. Temperature-dependent sheet resistances of TiN films.



FIG. S5. SEM images of (a) pristine TiN films, (b-e) TiN films immersed in HCl for 2, 3, 4, and 6 days, and (f-i) TiN films immersed in KOH for 3, 6, 8, and 9 days.



FIG. S6. HAADF-STEM image of the TiN films on  $Al_2O_3$  substrate immersed in HCl for (a) 6 days and (b) 7 days, respectively. The brighter region of around 30 nm was observed in both.



FIG. S7. (a) HAADF-STEM image of TiN films on  $Al_2O_3$  substrates immersed in HCl for 6 days, combined with the EDX mapping of Cl, Ti, N, Al, and O. (b) Enlargement of the brighter area as depicted in (a). (c) Atomic-resolution image of the TiN film at the interface of the film and the substrate as depicted in (a).

## II. ELECTROCHEMICAL FORMULA

The adsorption process of a Cl<sup>-</sup> ion is expressed as

$$\mathrm{TiN} + \mathrm{Cl}^- \to \mathrm{Cl}@\mathrm{TiN} + e^-, \tag{S1}$$

and according to the electrochemical theory<sup>1</sup>, the associated free energy of reaction ( $\Delta G_1$ ) at the standard condition (298.15 K, 1bar) is expressed as

$$\Delta G_1 = \Delta G_{\rm ad} - eU,\tag{S2}$$

where  $\Delta G_{ad}$  is the chemical part at the standard condition (298.15 K, 1 bar); U is the electrode potential with respect to the standard hydrogen electrode (SHE)<sup>1</sup>. In the DFT calculations,  $\Delta G_{ad}$  is defined as

$$\Delta G_{\rm ad} = E(\operatorname{Cl}@{\rm slab}) - E(\operatorname{slab}) - \frac{1}{2}[E(\operatorname{Cl}_2) - TS(\operatorname{Cl}_2)] - \mu(\operatorname{Cl}^-), \tag{S3}$$

where E(Cl@slab), E(slab), and  $E(Cl_2)$  are the electronic energies of Cl-adsorbed TiN(111) surface, a pristine TiN(111) surface, and a free Cl<sub>2</sub> molecule, respectively;  $TS(Cl_2)$  is the thermal correction to the energy of a standard gaseous Cl<sub>2</sub>, i.e., the freeenergy change of Cl<sub>2</sub> from 0 to 298.15 K<sup>2</sup>;  $\mu(Cl^{-})$  is the standard chemical potential aqueous Cl<sup>-</sup> ion<sup>3</sup>.

To indicate the stability of a Cl-substituted TiN(111) surface created after the ingression process, the Cl<sup>-</sup> ion in the solution is considered as the reference as that for the adsorbed surface (see Equation S1 above). There are two possible reaction paths considered here, and the corresponding reaction equations and free energies of reaction are described below.

Path (1): The substituted N anion escapes as a gaseous state, then we have

$$\mathrm{Ti}_{\mathrm{n}}\mathrm{N}_{\mathrm{n}} + \mathrm{Cl}^{-} \to \mathrm{Ti}_{\mathrm{n}}\mathrm{N}_{\mathrm{n}-1}\mathrm{Cl} + \frac{1}{2}\mathrm{N}_{2} + e^{-}$$
(S4)

and

$$\Delta G_2 = \Delta_{\rm f} G_2 - eU,\tag{S5}$$

where the chemical part  $\Delta_{\rm f}G_2$  is expressed as

$$\Delta_{\rm f} G_2 = E({\rm Cl}@{\rm slab}) - E({\rm slab}) - \frac{1}{2}[E({\rm Cl}_2) - TS({\rm Cl}_2)] + \frac{1}{2}[E({\rm N}_2) - TS({\rm N}_2)] - \mu({\rm Cl}^-).$$
(S6)

Path (2): The substituted N anion escapes as an aqueous  $NO_3^-$  ion, then we have

$$TiN + Cl^- + 3H_2O \rightarrow Ti_nN_{n-1}Cl + NO_3^- + 6H^+ + 6e^-$$
 (S7)

and

$$\Delta G_3 = \Delta_{\rm f} G_3 - 6k_{\rm B} T \cdot \ln(10) \cdot \mathrm{pH} - 6eU, \tag{S8}$$

where the chemical part  $\Delta_{\rm f}G_3$  is expressed as

$$\Delta_{\rm f}G_3 = E({\rm Cl@slab}) - E({\rm slab}) - \frac{1}{2}[E({\rm Cl}_2) - TS({\rm Cl}_2)] + \frac{1}{2}[E({\rm N}_2) - TS({\rm N}_2)] - 3\mu({\rm H}_2{\rm O}) - \mu({\rm Cl}^-) + \mu({\rm NO}_3^-)$$
(S9)

where  $\mu(H_2O)$  is the standard chemical potential of water (-2.458 eV)<sup>3</sup>, and  $\mu(NO_3^-)$  is the chemical potential of  $NO_3^-$  ion at  $10^{-6}$  mol/L, as calculated by  $\mu(NO_3^-) = \Delta \mu^0 + k_B T \cdot \ln([I])$ , with its standard counterpart  $\Delta \mu^0$  equal to -1.154 eV<sup>3</sup>.

The values of  $\Delta G_{ads}(O^*)$  and  $\Delta G_{ads}(OH^*)$  are calculated to indicate the adsorption stabilities of O\* and OH\* at different solution pHs and electrode potentials. The reaction path for O\* adsorption is written as:

$$H_2O + slab \to O@slab + 2H^+ + 2e^-,$$
(S10)

and the associated adsorption free energy is expressed as:

$$\Delta G_{\rm ads}(\mathcal{O}^*) = \Delta E_{\rm e}(\mathcal{O}^*) - T\Delta S(\mathcal{H}_2) + T\Delta S(\mathcal{H}_2\mathcal{O}) - 2k_{\rm B}T \cdot \ln(10) \cdot \mathrm{pH} - 2eU, \tag{S11}$$

where last two terms correspond to the two protons and two electrons involved in the reaction.  $\Delta E_e(O^*)$  is the chemical part for the energetic difference, i.e.,

$$\Delta E_{\rm e}({\rm O}^*) = E({\rm O}^{\otimes}{\rm slab}) - E({\rm slab}) - E({\rm H}_2{\rm O}) + E({\rm H}_2), \tag{S12}$$

where the equation of  $H^+ + e^- = \frac{1}{2} H_2$  at the standard condition (298.15 K, 1 atm, pH = 0, U = 0 V) has been used.

The reaction path for OH\* adsorption is written as

$$H_2O + slab \rightarrow OH@slab + H^+ + e^-,$$
 (S13)

and the associated adsorption free energy is

$$\Delta G_{\rm ads}(\rm OH^*) = \Delta E_e(\rm OH^*) - \frac{1}{2}T\Delta S(\rm H_2) + T\Delta S(\rm H_2O) - k_BT \cdot \ln(10) \cdot pH - eU, \tag{S14}$$

where the chemical part is expressed as

$$\Delta E_{\rm e}({\rm OH}^*) = E({\rm OH}@{\rm slab}) - E({\rm slab}) - E({\rm H}_2{\rm O}) + \frac{1}{2}E({\rm H}_2).$$
(S15)

## REFERENCES

<sup>&</sup>lt;sup>1</sup> L. -F. Huang, J. R. Scully and J. M. Rondinelli, Annu. Rev. Mater. Res., 2019, 49, 53–77.

<sup>&</sup>lt;sup>2</sup> M. W. Chase, *NIST-JANAF Thermochemical Tables, 4th ed.* (American Institute of Physics, New York, 1998).

<sup>&</sup>lt;sup>3</sup> A. J. Bard, R. Parsons, and J. Jordan, *Standard Potentials in Aqueous Solution*. (Marcel Dekker, New York, 1985).