# Supporting Information

for

# Microscopic evidence for dissociation of water molecules on cleaved $GaN(1\overline{1}00)$

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#### S1. LEED and STM after dosing water

The low electron energy diffraction (LEED) and scanning tunneling microscopy (STM) were taken on the cleaved GaN( $1\overline{1}00$ ) surface after dosing 0.9 L water molecules, as shown in Fig. S1. The diffraction pattern is similar to that of the clean surface, as shown in Fig. S1(a). The position of the diffraction spots are the same. Only the intensity changes. This indicates the same lattice of the surface structure but different scattering factor of the surface atoms which is likely due to the adsorption of the water molecules. The STM image also shows no clear different after dosing water, as shown in Fig. S1(b).



**Figure S1:** (a) LEED of the cleaved GaN(1100) surface after dosing 0.9 L water molecules. The electron kinetic energy for LEED is 150 eV. The  $(1 \times 1)$  lattice is marked as  $b_1$  and  $b_2$ . (b) STM on the same surface taken at 3.5 V, 100 pA.

## S2. Beam-induced dissociation

Figure S2 shows the XPS of O 1s and N 1s after pre-dosing 0.9 L water molecules in the dark environment on the cleaved GaN( $1\overline{1}00$ ) surface. Unlike the spectra taken simultaneously under water pressure, clear O 1s and peak 3 in N 1s are already observed on the surface with pre-dosed water molecules. It suggests that the reaction happens even without irradiation. Therefore, the beam-induced dissociation is excluded.

### S3. Similar reaction at RT and 130K

To test the reaction rate at low temperature, the sample was cooled to 130 K and cleaved at 130 K. The real-time XPS was then taken at 130 K. The behavior of the reaction is similar to that at room temperature, as shown in Fig. S3. The reaction ends at 25th to 27th minute.



Figure S2: XPS of O 1s and N 1s after pre-dosing 0.9 L water molecules in dark environments. The spectra were taken after irradiation for 3 minutes.

The slope in area fraction v.s. time plot are also similar to that at RT. According to Arrhenius equation, the relationship between the reaction rate coefficient k and the activation energy  $E_a$  is  $k = A \times e^{-\frac{E_a}{RT}}$ , where A is the frequency factor, R is the universal gas constant, T is the temperature. Therefore, the similar reaction rate at room temperature and at 130 K implies a much smaller activation energy  $E_a$  comparing to the thermal energy at 130 K (~ 11 meV).



**Figure S3:** (a) Real-time XPS of O 1s, N 1s, and Ga 3d at 130 K. The water molecules were dosed at the 12th min with pressure of  $1 \times 10^{-9}$  torr. (b) Area fraction of O1s. (c) Area fraction of N 1s. The dash lines mark the time when the water molecules were dosed.

#### S4. Density functional calculations of different models

To compare the Ga 3d spectrum from the experiments, we also calculated different models. Figure S4 shows two other types of water molecules on top of the nonpolar GaN(1 $\bar{1}00$ ) surface. One is the surface with non-dissociated water molecules. Another one is the surface with the formation of N-OH and Ga-H bonds. Comparing to the clean surface, the partial density of states (PDOS) of Ga 3d shows almost no change in the model with non-dissociated water on the surface. The total energy is 13.36 eV (1.48 eV/water molecule) higher than that of the dissociated water model. The model with N-OH and Ga-H on the surface shows a relative narrower Ga 3d PDOS for ~ 0.4 eV. Although this model also has similar tendency as the experiment, this model is unstable from the theoretical point of view. The total energy of this model is 30.22 eV (3.36 eV/water molecule) which is much higher than that of the N-H, Ga-OH model which is calculated as 0 eV. Therefore, the N-OH, Ga-H model is not adopted for the experiment even it shows similar tendency because the N-OH, Ga-H is unstable in the calculations.



Figure S4: Models of (a) the non-dissociated water molecules and (b) with the formation of N-OH, GaH bonds on top of the nonpolar GaN( $1\overline{1}00$ ) surface. The relative total energy was calculated by setting that of the dissociation water model as zero energy. (c) and (d) show the PDOS from different Ga-N layers of the models in (a) and (b), respectively. The dashed line marks the energy position of the Ga 3*d* peak of the 5th Ga-N layer which is referred to the bulk peak.