Photo-induced selective etching of GaN nanowires in water - Supporting Information

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In Fig. 1 a numerical simulation of the electric field distribution around and inside of a GaN nanowall is depicted. For the simulation, a pitch of 1000 nm, height of 600 nm and thickness of 200 nm have been assumed, which is similar to the dimensions of the nanowalls displayed in Fig. 7 of the main article. The simulation plane is a profile slice through the wall. In this configuration, the electric field within the nanowall is almost exclusively concentrated in the upper part. Consequently, the charge carrier concentration is highest in this region, leading to a locally enhanced photochemical decomposition rate.

Figure 2 depicts p-type doped GaN NWs grown on sapphire (a) before and (b) after illumination with a 266 nm laser in DI water for 5 min. c) Low temperature PL spectrum of the same NW array at 5 K.

Figure 3 shows GaN NWs covered with different oxide shells before and after exposure to 266 nm light with an intensity of 9.5 kW/cm² for 5 min in DI water. The doping concentration is estimated to $10^{19}$ 1/cm³. For these NWs, only a slight change in morphology but no significant decomposition is observed. Likely, the enhanced stability originates from the reduced hole concentration at the surface due to the upward sbb in p-type GaN. In Figure 2c, the corresponding low temperature PL spectrum is depicted. The A’X emission appears at 3.467 eV, which is a typical value for p-GaN. The dominant sub-band gap emission is the donor-acceptor pair luminescence between about 2.6 and 3.3/eV. Only minor traces of stacking fault related emission is observed.

Fig. 1 Simulated electric field in a GaN nanowall array immersed in water under 341 nm illumination. The nanowalls have a pitch of 1000 nm, a height of 600 nm and a thickness of 200 nm.

Fig. 2 SEM images of p-type doped GaN NWs on sapphire (a) before and (b) after illumination with a 266 nm laser in DI water for 5 min. c) Low temperature PL spectrum of the same NW array at 5 K.

Fig. 3 SEM images of GaN NWs with 50 nm Ga$_2$O$_3$ (green framed) and 3 nm Al$_2$O$_3$ (red framed) shells before and after exposure in DI water.
Ga$_2$O$_3$ shells effectively hinder the decomposition of the GaN NWs and, thus, the morphology of the NWs remains unchanged before and after photochemical etching.

In Fig. 4a, a numerical simulation of the elastic energy density (EED) distribution in a hexagonal GaN NW, assuming a small amount of compressive surface strain, is depicted. The existence of surface strain in GaN due to surface reconstruction is likely and is in agreement with the literature on related semiconductors.$^2,3$ The corners where the EED accumulates, coincide with the regions where the etch rate is lowest (Figs. 1c main text and 4a). We hypothesize that this correlation might be induced by an influence of strain and geometry on the electronic band structure of GaN NWs.$^4,5,6$ Following this idea, 2D simulations of the A VB in a hexagonal GaN NW were performed (Fig. 4b). In accordance with the literature and measurements performed in our group on m-plane GaN, the sbb was fixed to 0.55 eV at the NW sidewalls.$^7$ Three regions of interest can be identified (marked with red, green, and blue lines in the top NW corner in Fig. 4b). In the red region, a band crossing between A and B VBs occurs due to a downward/upward step, respectively (Fig. 4b), which is a well known consequence of strain on the VB order of GaN.$^4,5,6$ In the green region, a significant decrease in energy of the A VB is predicted, followed by a steep increase towards the surface in the blue region. Note, that the small features in the blue and green regions are a result of the finite step width of the simulation grid. This complex behavior of the A VB, which is the uppermost VB in unstrained regions of the NW, could slow the drift of holes towards the corners as they either have to perform an inter-VB transition from A to B and back to stay in the topmost VB or have to overcome the energetic steps. However, the relaxation towards the energetically highest VB takes place in the order of few ps$^8,9$, therefore the slow-down caused by the energetic steps in the VBs are unlikely to be the sole reason for the slower etching rates of the NW corners. A further contribution originates from the different slope of the VBs close to the NW edges compared to the vicinity of the side facets. Following the black arrow in Figure 4b, the relative strain-free regions exhibit a steeper increase of the valence band energy towards the surface as the strained ones do. Therefore, a deflection towards the sidewalls is likely to be the preferential route for holes to reach the surface and the reduced flux of holes in the corners would locally reduce the etch rate.

Notes and references