Supporting Information

**Silicon-supported aluminum oxide membranes with ultrahigh aspect ratio nanopores**

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**Experimental Section**

*Electropolishing process*

First, Al sheets (4N Purity, 3 cm x 3 cm, ESPI Metals, USA) were cleaned under sonication in acetone, 2-propanol and ethanol for 5 min in each solvent, subsequently. Afterwards, the Al was abundantly rinsed with deionized (DI) water. Prior to a two-step anodization, electrochemical polishing was conducted potentiostatically at +19 V at 15 °C for 5 min under vigorous stirring in a mixture of perchloric acid (HClO₄, Sigma) and ethanol (C₂H₅OH, Sigma) with 1:3 volume ratio, followed by an abundant rinsing step with DI water. A mirror-like surface was obtained indicating a decrease in the surface roughness of the Al sheet.

*Anodization process for MA and PA-SAAO with ultrahigh-aspect ratio nanopores*

To prepare an MA-SAAO with ultrahigh-aspect ratio pores, a two-step anodization process was conducted as follows. The first anodization was performed in 0.3 M oxalic acid (H₂C₂O₄, > 99 %, Sigma) at a constant potential of +40 V, at 10 °C for 15 hrs. During this entire anodization process, vigorous stirring was used to avoid excessive heat at the metal-oxide and oxide-electrolyte interfaces due to the exothermicity of the oxidation process. The formed
porous anodic alumina (Al₂O₃) was then chemically etched in a solution containing 1.8 wt% chromic acid (H₂Cr₂O₇, Sigma) and 6 wt% phosphoric acid (H₃PO₄, > 98%, Sigma) at 60 °C for 6 hrs to obtain a well-aligned concave patterned Al surface. The second-step anodization was further processed on this pre-patterned surface for 15 hrs at the same conditions as the first-step anodization, which gives a thickness of 50 μm. For the preparation of a PA-SAAO with ultrahigh aspect ratio pores, an electropolished sample was subject to a first mild anodization step in 0.3 M sulfuric acid (H₂SO₄, 95.0-98.0%, Sigma) at the constant potential of +25 V at 0 °C for 15 hrs under vigorous stirring. After etching the obtained layer of anodic alumina (Al₂O₃) in the previously mentioned etching solution, pulsed anodization (PA) was conducted in 0.3 M sulfuric acid at 0 °C. Each cycle of the pulse consisted of a mild anodization (MA) step with a potential of +25 V for 900 s and a hard anodization step (HA) with a potential of +35 V for 2.5 s including a ramp time of 500 ms each with a rate of 20 V s⁻¹. 27 cycles were used for the PA process.

**Au to Au layer thermal compressive bonding process**

A cleaning process was performed both for an SAAO sample and a Si wafer (crystal orientation (111), p-type, resistivity 0.005 Ω m - 0.02 Ω m, Prolog Semiconductor). An Al sheet was sonicated for 5 min in acetone, 2-propanol and ethanol, and then rinsed with DI water to remove organic residuals. In addition, a Si wafer was sonicated for 10 min in acetone, isopropanol and, finally with piranha solution. The piranha solution consisted of 30% hydrogen peroxide (H₂O₂, 31%, Sigma) and 70% sulfuric acid (H₂SO₄, 95.0-98.0%, Sigma). After thorough rinsing in DI water and after a drying process, plasma etching was conducted for 5 min at 600 W to remove inorganic residuals. A Ti adhesive layer of 10 nm and a Au layer of 500 nm were subsequently deposited by means of e-beam evaporation (Edwards E306A, Edwards, UK) on the surface of anodic aluminum oxide (AAO) side and Si at the vacuum level of $1 \times 10^{-6}$ Torr, respectively. Then, the Au-coated silicon wafer was diced into
small chips (3.5 cm × 3.5 cm). Afterwards, the anodized Al was positioned onto a Si chip so that the Au layers were facing to each other. Finally, the two parts were compressively bonded using a wafer bonder (AML AWB, AML, UK) at $1 \times 10^{-5}$ Torr, 320 °C, and a mechanical pressure of 5 MPa for 15 min.

### Al and barrier layer etching processes

The remaining top Al layer was completely etched in an Al etchant solution consisting of 0.1 M copper chloride (CuCl$_2$·6H$_2$O, Sigma) and 6.1 M hydrochloric acid (HCl, 37%, Sigma). The exposed barrier layer was then physically etched using RIE (RIE 76, Oxford Instruments Plasmalab 80) at the chamber pressure of 12 mTorr, CF$_4$ flow of 40 sccm, O$_2$ flow of 5 sccm, and a power of 200W. For the etching duration, we used a cycle consisting of 3 min of etching and 5 min of cooling to avoid surface overheating. A total of ten cycles was used for an MA-SAAO sample and seven cycles for the HA-SAAO sample. After this barrier layer etching process, brief oxygen plasma etching was performed at a vacuum pressure of 25 mTorr and O$_2$ flow of 25 sccm to render the surface hydrophilic.

### Electrodeposition of Ni

The Ni electrolyte contained 300 g l$^{-1}$ of nickel sulfate heptahydrate (NiSO$_4$·7H$_2$O, >99%, Sigma) and 45 g l$^{-1}$ boric acid (H$_3$BO$_3$, >98%, Sigma). The pH was adjusted to 5.0 using sodium hydroxide (5 M NaOH). During electrodeposition, SAAO samples and platinized titanium served as working and counter electrodes, respectively. For MA-SAAO sample, Ni was galvanostatically electrodeposited using a power supply (Autolab PGSTA302N, Ecochemie, The Netherlands) at a constant current density of $-2$ mA cm$^{-2}$ at RT for 1 h. For the PA-SAAO sample, Ni was galvanostatically deposited at a constant current density of $-3$ mA cm$^{-2}$ at RT for 1 h. All electrodeposition steps were performed under moderate stirring (about 200 rpm).
**Characterization**

All SEM images were taken using a field-emission scanning electron microscope (FE-SEM, Zeiss Ultra 55, Carl Zeiss, Germany). For this, the samples were prepared as follows: The specimens for cross sectional views of our MA and PA-SAAO samples were achieved by a simple mechanical breaking method. The released NWs were obtained by suspending and drying a small volume of Ni NWs in suspension on a conductive substrate.

Cross-sectional imaging was performed by a focused ion beam (FIB) SEM. To achieve this, an initial FIB milling at 1 μA was conducted to create a large cross-section by plasma FIB (Tescan, Fera3 Xe-Plasma FIB-SEM) followed by smoothing cuts using milling currents in the range of 300 pA to 1.5 nA (Zeiss, NVision 40 FIB-SEM). Prior to FIB analysis, the sample was sputtered with 20 nm of Au/Pd (BALTEC SCD-050) and mounted on a SEM stub using silver paint.
**Fig. S1** A top-view SEM image of a cracked PA-SAAO sample.

**Fig. S2** A cracked PA-AAO; after etching Al substrate without preceding bonding process.