Electronic Supplementary Material (ESI) for ChemComm.
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Supplementary Information:

Visualizing Anisotropy in the Surface Oxidation of Germanium by Wet Etching of Patterned Nanowedges: Proof of Concept

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Experimental Section:

Ge surface preparation: All single-crystal Ge (100) and (110) wafers (AXT Inc.) used in this work were n-type and Sb-doped with a resistivity of 0.05-0.08 Ω-cm. Samples were pre-cleaned[1-2] through a sequential process: 1) 5 min immersion in ozone bath with 8 ppm concentration, 2) 3 min of rinsing in an ultra-pure water (UPW), 3) 5 min of immersion in 6M HCl, 4) 3 min of rinsing in an ultra-pure water (UPW), 5) nitrogen (N_2) blow drying.

Chemicals were used as-received from Sigma Aldrich and were of p.a. quality: 37% HCl (12.0 M), 96% H_2SO_4 (18.0 M), and 30% H_2O_2 (9.7 M).

Ge test model fabrication: Patterned Ge nanowedges were fabricated by a lithographic technique with the use of a dedicated mask as shown in Figure S1. The design of this test model was composed of 32 equally spaced (~5.6°) nanowedges, which were arranged in a 360° radial pattern. The diameter size of the circular patterned wedges was approximately 4 µm. The nanowedges were 45-80 nm wide (decreasing width from outer to inner part), 800 nm long, and 550 nm high. Prior to the patterning step, an epitaxial layer of nearly 600 nm of undoped Ge was deposited at 440˚C using GeH_4 as a precursor on a p-type boron-doped silicon (Si) wafer in H_2 environment. After, it was annealed at 850˚C for 3 min in H_2. Then, a 30 nm thick silicon-rich nitride (SiN) masking layer was deposited by low pressure chemical vapor deposition (LPCVD) at 690˚C. On top of that, an APF™ (Advanced Patterning Film, Applied Materials) layer of 160 nm was deposited via plasma enhanced chemical vapor deposition (PECVD). 193nm immersion lithography technology was used to transfer the pattern onto the hard mask. After APF and SiN hard mask were opened with O_2/Ar and CF_4/CH_2F_2 plasmas, respectively, the Ge wedges were dry etched with SF_6 at 5mTorr in a N_2 ambient condition. The APF was stripped in O_2 at 10mTorr. Lastly, hydrofluoric acid (HF) (2%) solution was used to remove any dry-etch residues and/or oxides on the nanowedges.

Ge etching kinetics: Etching experiments were performed in a cleanroom facility using a rotating disk electrode (RDE). A Kalrez o-ring with an exposed area of 2.01 cm^2 was used to prevent

leakage on backside and edges that can interfere etch rate measurement. The etch rate was determined by measuring the total amount of dissolved ^{72}Ge with inductively coupled plasma–mass spectrometry (ICP-MS, Agilent 7500cs). This technique enables detection of substrate loss at sub-monolayer level. The measurement error of the etch rate is <10% under these conditions.

Ge surface characterization: Surface morphology of the etched Ge samples was examined by field-emission scanning electron micrsocope (SEM, Omicron).

The synchrotron photoemission studies were carried out at the undulator beamline UE56/2 PGM1 of the BESSY II storage ring, which provides photons in the energy (hυ) range of 100 - 1100 eV. The photoemission spectra were measured at highest possible surface sensitivity. The valence band and Ge3d core levels were measured with 100 eV excitation energy. For Cl2p and O1s core levels, 250 eV and 600 eV were used, respectively. All spectra were measured at normal emission. Core-level spectra were fitted with Voigt functions after Shirley background subtraction using IGOR Pro Software (Wavemetrics Inc.). The spectra were obtained using the Phoibos 150 (SPECS) energy analyzer of the experimental system solid/liquid analysis system (SoLiAS)[3] permanently housed at BESSY.

For the SXPS measurements, Ge (100) and (110) samples were prepared *in situ,* under a continuous flow of etchant, using a dedicated etching chamber of the SoLiAS[3] end station. This glass chamber, purged with dry and carbon-free Ar gas, is directly connected to a buffer chamber that permits the transfer of the sample into the ultrahigh vacuum (UHV) for subsequent photoemission analysis without exposure to ambient conditions. All Ge (100) and (110) samples used for surface characterizations were Ar gas blow-dried after each etching treatment. No water rinse was applied to minimize surface modification after treatment.[2]

Supplementary Figures:

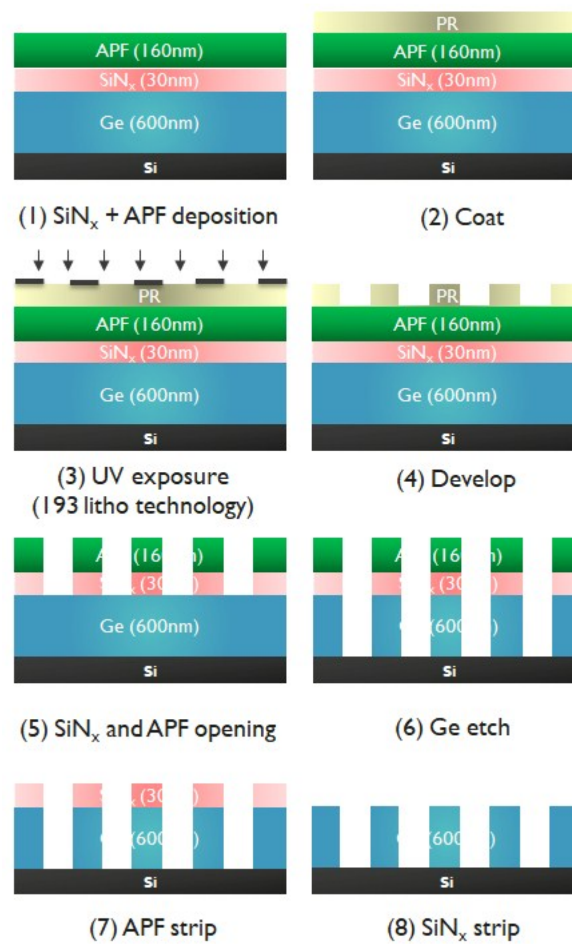

Figure S1. Schematic diagram of Ge nanowedges fabrication.

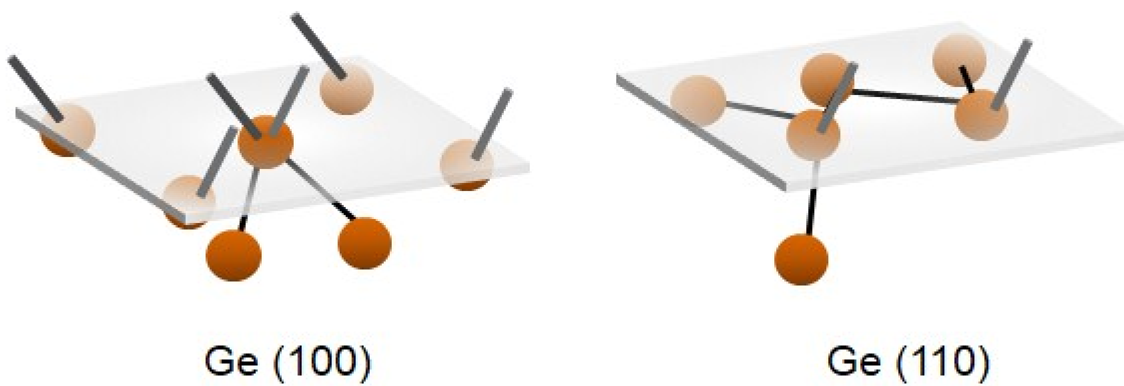

Figure S2. Ball and stick model of Ge (100) and (110).

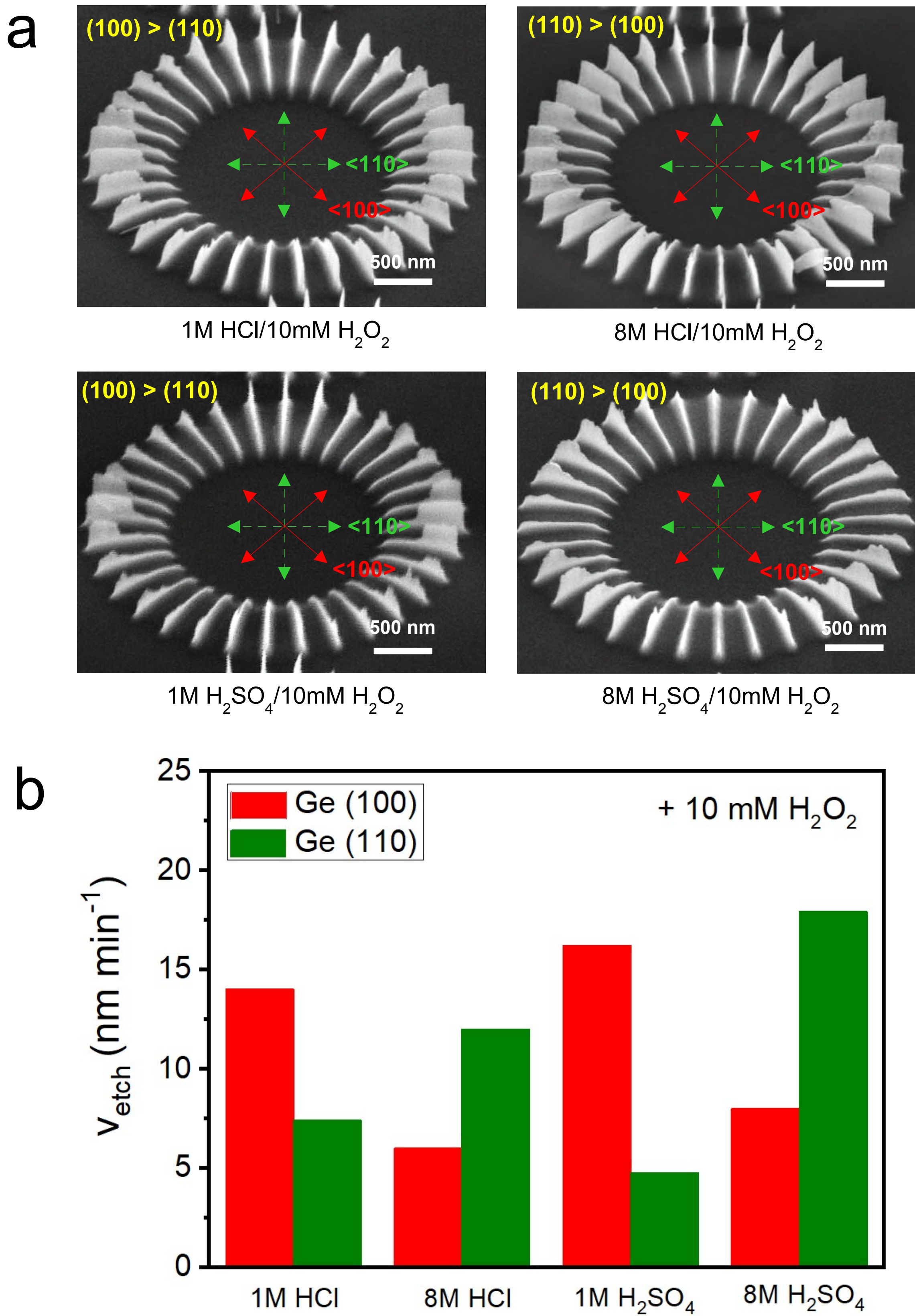

Figure S3. a) Scanning electron microscopy (SEM) images of Ge nanowedges etched in various acidic solutions with their corresponding b) etch rate measured using inductively coupled plasma mass spectrometry (ICP-MS).

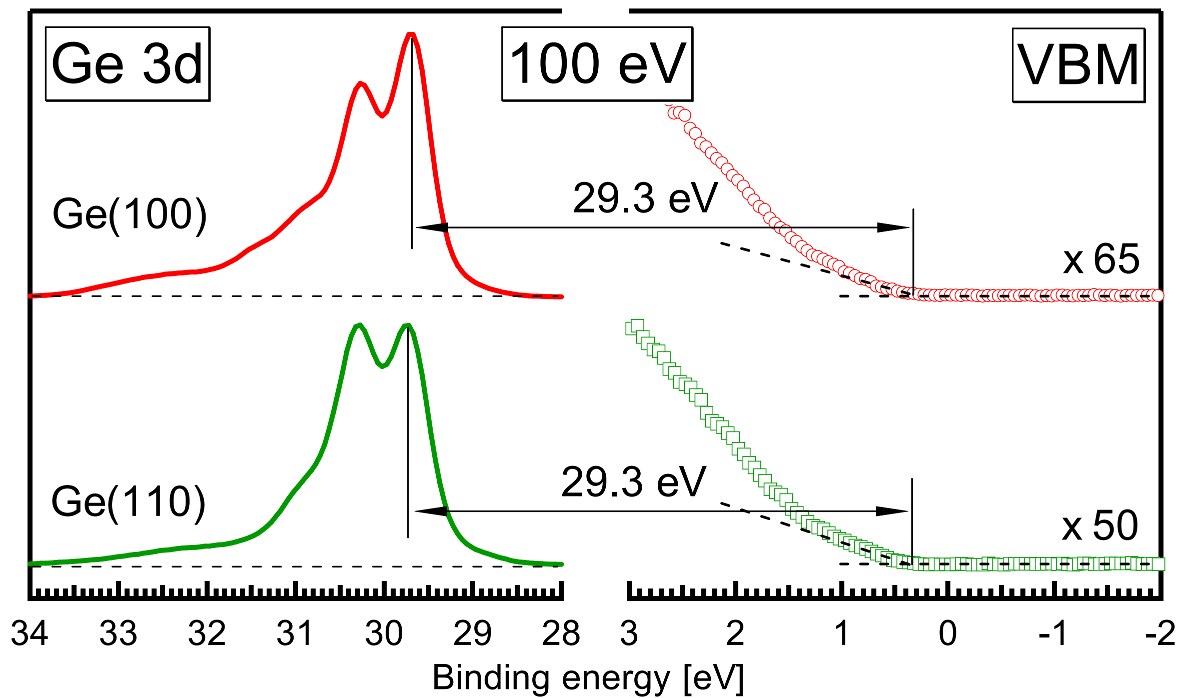

Figure S4. Binding energy difference between Ge3$d_{5/2}$ and valence band maximum (VBM) measured with the excitation energy at 100 eV for Ge (100) and (110) etched in 1 M HCl/10 mM H_2O_2.

Supplementary Table:

Table S1. Spectral components of Ge (100) and Ge (110) before and after etching in 1 M HCl/10 mM H_2O_2

Samples	**Coverage (ML ± 0.05ML)**				
	Ge-Cl	Ge^{1+}	Ge^{2+}	Ge^{3+}	Ge^{4+}
Ge (100) reference	-	0.37	0.53	0.99	1.19
Ge (100) etched	0.11	0.45	0.13	0.04	-
Ge (110) reference	-	0.28	0.62	2.26	2.17
Ge (110) etched	0.38	0.20	0.10	0.04	-

References:

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Acknowledgments

This work is part of the imec Industrial Affiliation Program on III-V/Ge devices. The authors acknowledge Screen Semiconductor Solutions Co. Ltd., Entegris ATMI, Kurita and Fuji Film Electronic Materials for their contributions to the Joint Development Program. We thank Helmholtz-Zentrum Berlin (HZB) for the allocation of synchrotron radiation beamtime. We also would like to thank Frank Holsteyns for management support.