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Towards the Epitaxial Growth of Silver on Germanium by Galvanic Displacement

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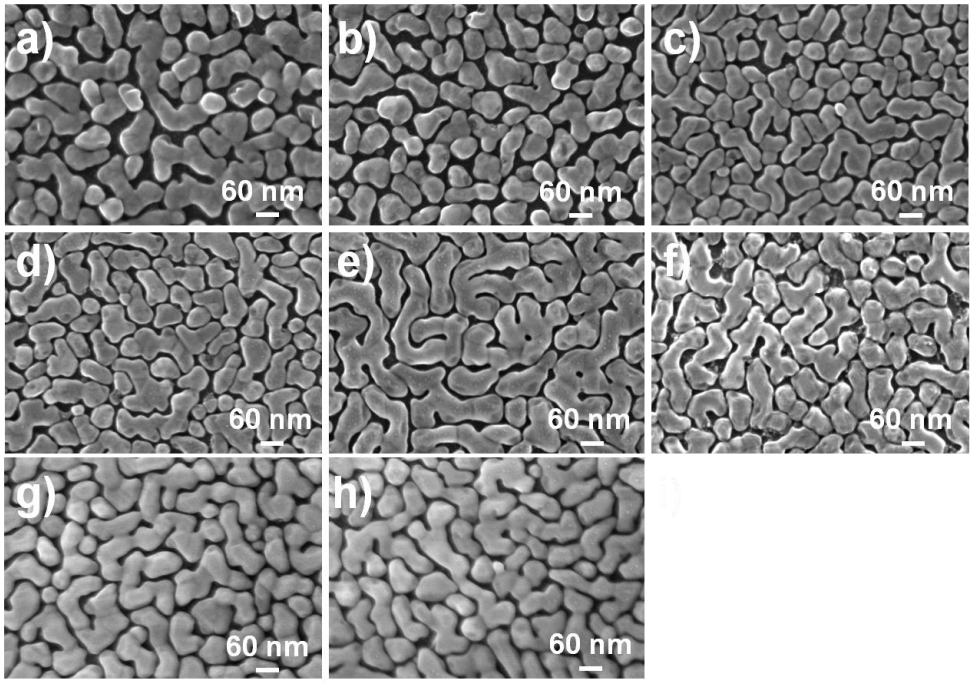

Figure S.1. Plan view scanning electron micrographs for silver galvanically displaced on Ge(111) surfaces. The silver nanostructures are formed after a 15 min immersion of Ge(111) shards in 0.5 mM $AgNO_3$ (aq) + x% of HF (aq); (a) x = 0, (b) x = 0.1, (c) x = 0.25, (d) x = 0.5, (e) x = 3, (f) x = 4, (g) x = 5, and (h) x = 6%.

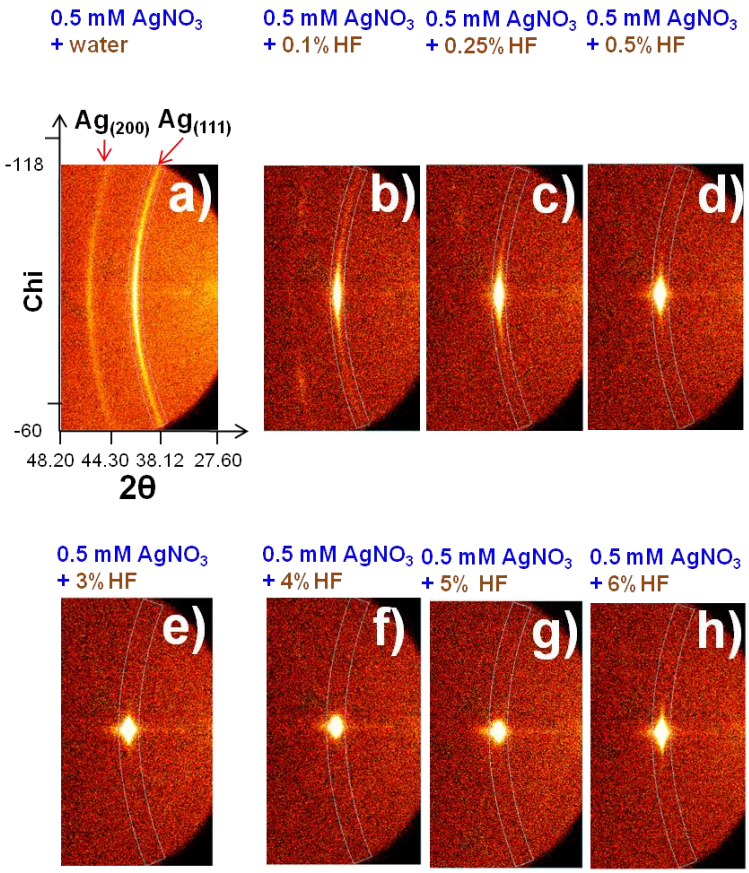

Figure S.2. XRD 2D frames obtained for silver galvanically displaced on Ge(111) surfaces. The silver films are formed after a 15 min immersion of germanium shards in 0.5 mM $AgNO_3$ (aq) + x% of HF (aq): (a) x = 0, (b) x = 0.1, (c) x = 0.25, (d) x = 0.5, (e) x = 3, (f) x = 4, (g) x = 5, and (h) x = 6%.

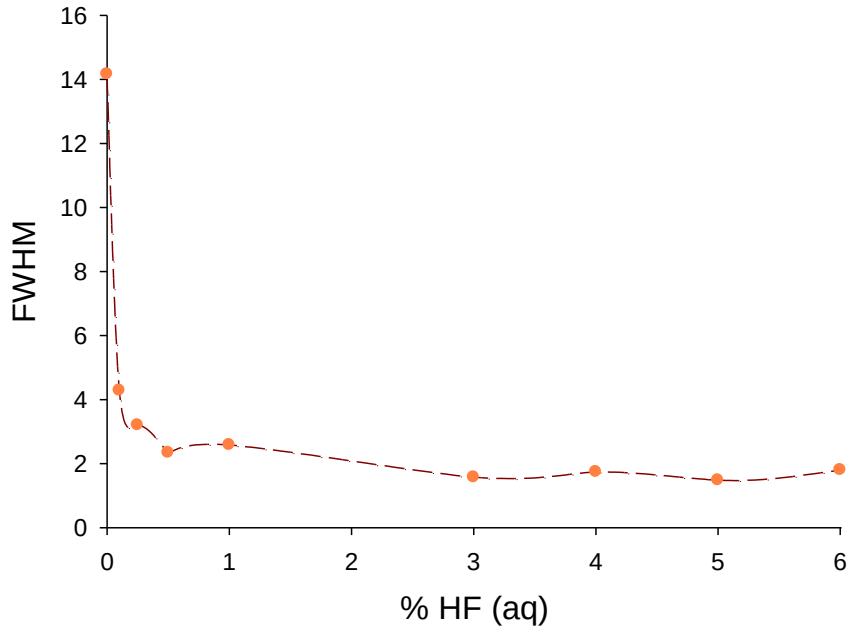

Figure S.3. The plot shows the change of the FWHM values, of the (I-Chi) peaks observed by integrating the diffraction intensity at $2\theta = 38.12^{o}$, Ag(111), along with chi, versus HF concentrations.

It is worth mentioning that the FWHM was found to be dependent on the concentration of HF in solution; FWHM decreases with increased concentrations of HF, see Supporting Information. Hence, it can be revealed that HF (aq) plays an important role in etching of the germanium oxide products formed during the galvanic displacement process, and thus allows for direct contact between silver films and the underlying germanium surfaces and results in the growth of large fraction of Ag(111) planes parallel to the substrate surface. The growth of silver on germanium surfaces in the absence of an oxide etching agent can occur spontaneously, see Supporting Information. The grown layer, however, may have different crystallographic

properties resulting from shading the substrate crystallographic identity by the existence of an interfacial oxide layer.

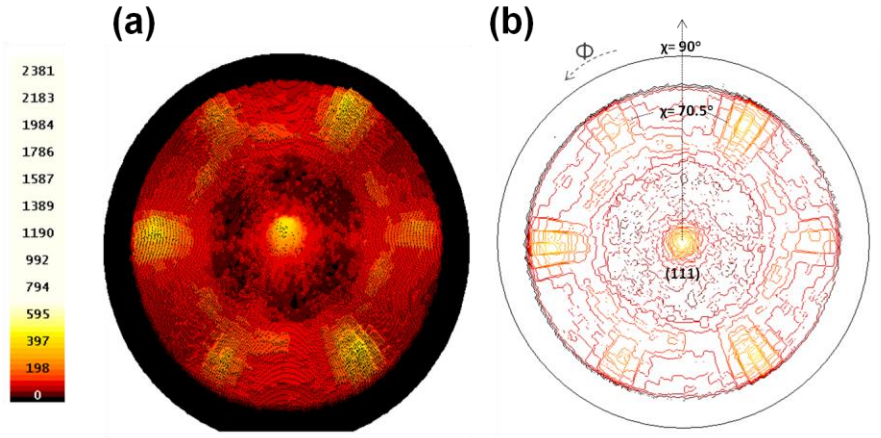

Figure S.4. (111) X-ray pole figures for Ag films, on Ge(111) substrates, produced after a 15 min immersion of the germanium substrates in 0.5 mM $AgNO_3$ (aq) solution containing 5% HF (aq) (a, b). The (111) surface and contour pole figures are represented in (a) and (b), respectively. The pole figures were obtained by setting 2θ equals to the angle of diffraction from the Ag(111) planes (2θ = 38.12^o) and collecting the diffraction intensity while rotating the sample azimuthally at different tilting angles (χ).

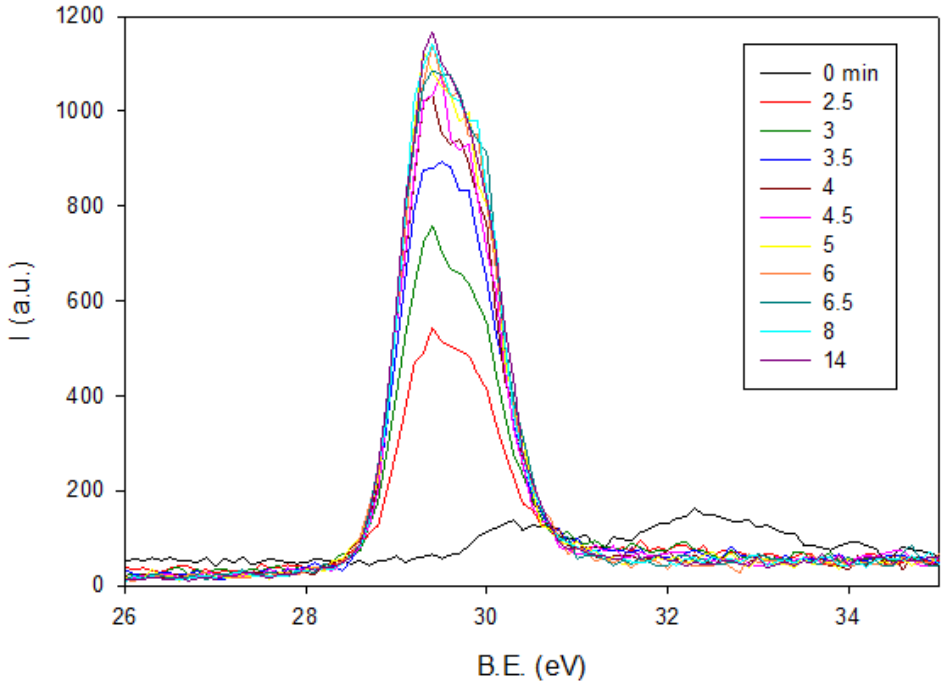

Figure S.5. Ge 3d XPS spectra of Ag/Ge(111), formed by immersion in 0.5mM $AgNO_3$+ 5% HF, after Ar^+-sputtering at different intervals of time.

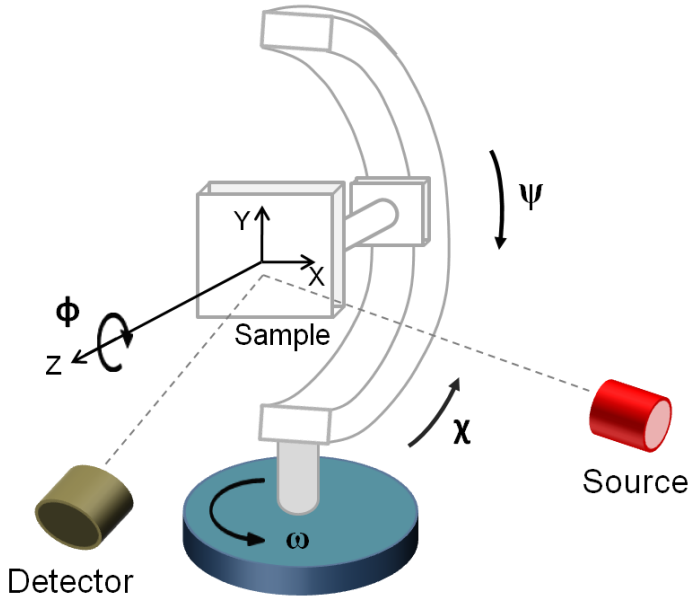

Figure S.6. Schematic diagram showing the experimental set up used in the in- and out-of-plane orientation analyses by X-ray diffraction. The pole figure was constructed by rotating the sample 360^{o} along the azimuthal axis "Φ" at different chi "χ" angles; $\chi = 90^{o} - \psi$. The sample was aligned vertically as shown in the figure at $\psi = 90^{o}$ ($\chi = 0^{o}$). The rocking curves were measured by fixing the detector position at the required 2θ and rocking the sample along the ω axis.[1]

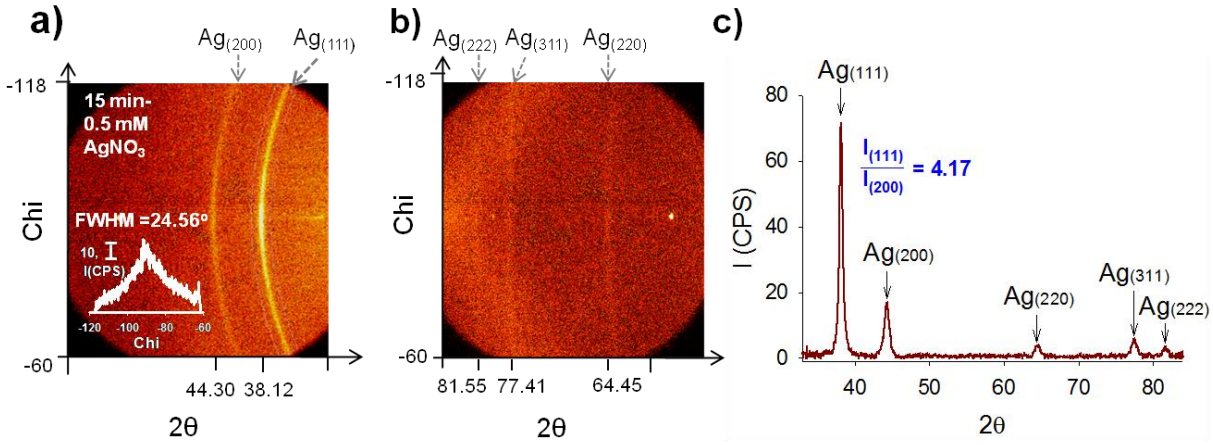

Figure S. 7. XRD data observed from silver nanostructures on Ge(111) prepared after a 15 min immersion of the germanium shards in 0.5 mM $AgNO_3$. (a, b) 2D XRD frames observed in the 2θ range of 27.6-48.2°, and 60.9 – 85.83°, respectively. (c) θ-2θ scan.

The growth of silver on germanium surfaces in the absence of an oxide etching agent can occur spontaneously, see supporting information.[2] The epilayer, however, may have different crystallographic properties resulting from shading the substrate crystallographic identity by the existence of an interfacial oxide layer. To explore the silver films grown from 0.5 mM $AgNO_3$ (aq) solution, we carried out XRD diffraction analyses (Figure S.7). The 2D XRD frames in Figure S.7a and S.7b show Debye diffraction rings from five silver planes at 2θ = 38.12°, 44.30°, 64.45, 77.41, and 81.55° corresponding to Ag(111), Ag(200), Ag(220), Ag(311), and Ag(222), respectively.[3] Debye diffractions rings indicate lower degrees of alignments, vide supra. The Debye diffraction ring observed from Ag(111) planes, for example, show a non uniform distribution intensity along the ring as shown from the intensity-chi plot inserted in Figure S.7a; the observation of a peak, however, reveals that the film is not polycrystalline and has a higher degree of alignment. The XRD θ-2θ scan (Figure S. 7c) shows five diffraction peaks

corresponding to Ag(111), Ag(200), Ag(220), Ag(311), and Ag(222).[3] The intensity ratio of Ag(111) to Ag(200) planes is 4.17, which is greater than the value of 2.21 observed for powder diffraction (JCPDS tables).[3] The high intensity ratio points to the oriented nature of the silver film on the germanium surface (fiber textured): The silver film has grown with a large fraction of (111) planes parallel to the Ge(111) surface.

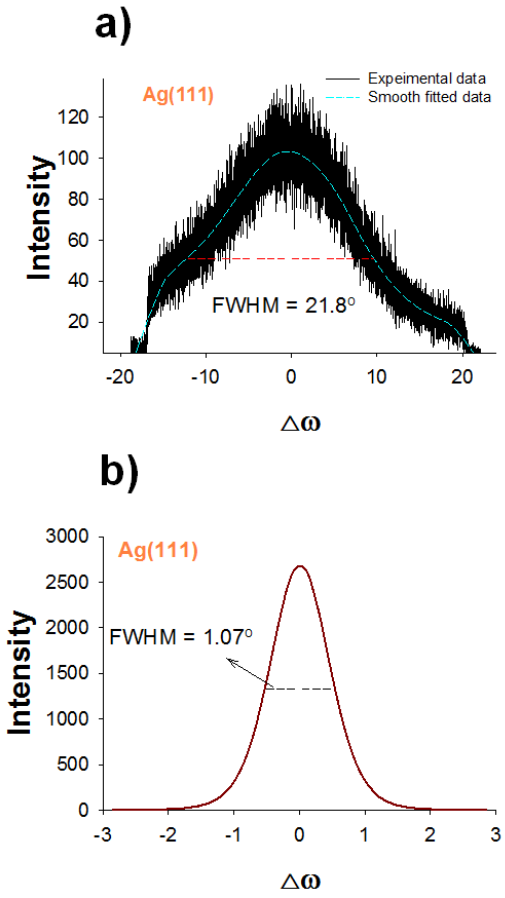

Figure S.8. X-ray rocking curves for Ag(111) from silver films prepared after a 15 min immersion of germanium substrates in 0.5 mM $AgNO_3$ (aq) (a), and in a mixture of 0.5 mM $AgNO_3$ (aq) + 5% HF (aq) (b).

The concept of mosaicity (deviated orientation of the grains along the out-of-plane direction) has been used to describe the ideality of single crystals. Single crystals are considered as small building blocks that may extend in a non-perfect periodicity from one side of the crystal to the other. Out-of-plane mosaicity can be investigated from the FWHM of rocking curves. Figures S.8a, and S.8b are the rocking curves for silver films-on-germanium prepared from solutions containing 0.5 mM $AgNO_3$ (aq) in the presence of 0 and 5% HF (aq), respectively. The FWHM observed for silver film grown in the presence of 5% HF (aq) is 1.07^o as compared to 21.8^o in the absence of HF. The low mosaic spread, low FWHM value, observed in the presence of 5% HF (aq) is indicative of a higher degree of alignment of the silver film with respect to the germanium surface. Such behaviour may be a result of the simultaneous etching of the germanium oxide product formed during the galvanic displacement process, allowing direct contact between the metallic silver and the underlying germanium surface.

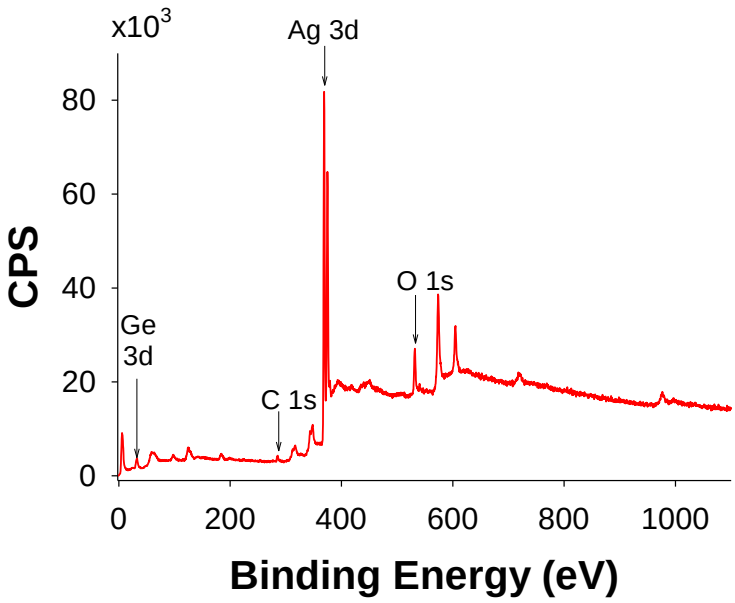

Figure S9. Survey scan of Ag on Ge(111) from 1 to 1200 eV. The Ag 3d, Ge 3d, C 1s and O 1s peaks are labeled.

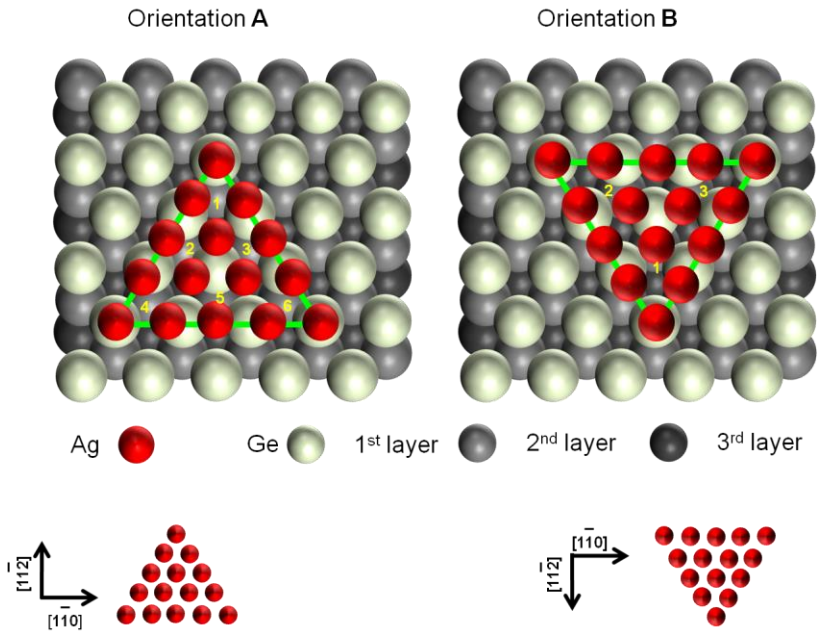

Figure S.10. Atomic model of Ag/Ge interface showing A and B orientations, both of which are rotated by 180^{o} with respect to the other. A orientation is more preferred as to the existence of six Ge atoms in the second layer, which provide more interaction with silver epilayer. In the case of B orientation, only three Ge atoms are exposed, and as result less preferable.

References

(1) Sayed, S. Y.; Buriak, J. M. *ACS Applied Materials & Interfaces* **2010**, *2 (12)*, 3515.
(2) Aizawa, M.; Cooper, A. M.; Malac, M.; Buriak, J. M. *Nano Letters* **2005**, *5*, 815.