

Block Copolymer-Templated Chemistry on Si, Ge, InP and GaAs Surfaces

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Experimental Procedures

Pretreatment of wafers

Silicon. Si(100) wafers (p-type, Ga doped, 0.01-0.02 ohm-cm, 500 μm thickness), purchased from Addison Engineering were initially washed in a methanol ultrasonic bath for 10 min. The wafers were then immersed in a hot solution of $\text{H}_2\text{O}_2\text{:NH}_4\text{OH:H}_2\text{O}$ (1:1:5) and next in another hot solution of $\text{H}_2\text{O}_2\text{:HCl:H}_2\text{O}$ (1:1:6) to remove organic contamination. After each cleaning step, the wafers were thoroughly rinsed with DI water (18 M-ohm, Barnstead Nanopure water) and dried with nitrogen.

Germanium. Ge(100) wafers (p-type, Ga doped, 0.018-0.036 ohm-cm, 500 μm thickness) were purchased from Umicore. The wafers were degreased in a methanol ultrasonic bath for 10 min, in boiling dichloromethane for 10 min, and then a methanol ultrasonic bath for 10 min. The oxide layer was removed by a solution of $\text{NH}_4\text{OH:H}_2\text{O}$ (1:4).^{1,2} After etching, the wafers were thoroughly rinsed with DI water.

Indium Phosphide. InP (100) wafers (p-type, S doped, carrier density $4.6 \times 10^{18} \text{ cm}^{-3}$, 0.001 ohm-cm, 500 μm thickness) were purchased from Crystacomm. The wafers were degreased in hot acetone for 10 min and a methanol ultrasonic bath for 10 min and were then thoroughly rinsed with methanol and dried with nitrogen.

Gallium Arsenide. GaAs(100) wafers (p-type, Zn doped, carrier density $1.5 \times 10^{18} \text{ cm}^{-3}$, 0.027 ohm-cm, 400 μm thickness) were purchased from EL-CAT. The wafers were degreased in hot acetone for 10 min and a methanol ultrasonic bath for 10 min. They were then thoroughly rinsed with methanol and dried with nitrogen.

Block copolymers

Block copolymers were purchased from Polymer Source, Inc. They were used without purification prior to use. In all cases, the polystyrene-block-poly(4-vinylpyridine) (PS-

P4VP) was dissolved in toluene at 70°C to make a 4-6 mg/mL solution and allowed to cool to room temperature.^{3,4}

Deposition 1. For deposition method 1, AgNO₃ or HAuCl₄ was dissolved in a toluene solution of the block copolymers by stirring at least for 48 h. The molar ratio of Ag⁺ or Au³⁺ to the pyridines in the P4VP block is 0.3:1. 10 µl of the metal loaded polymer solutions were spin coated on a 7 mm² wafer at 2000 rpm for 1 min under an inert atmosphere nitrogen environment (located within a Vacuum Atmospheres glove box). In 10 min, the polymer was removed by ultrasonication in neat toluene for 5 min, and the samples dried under a nitrogen stream.

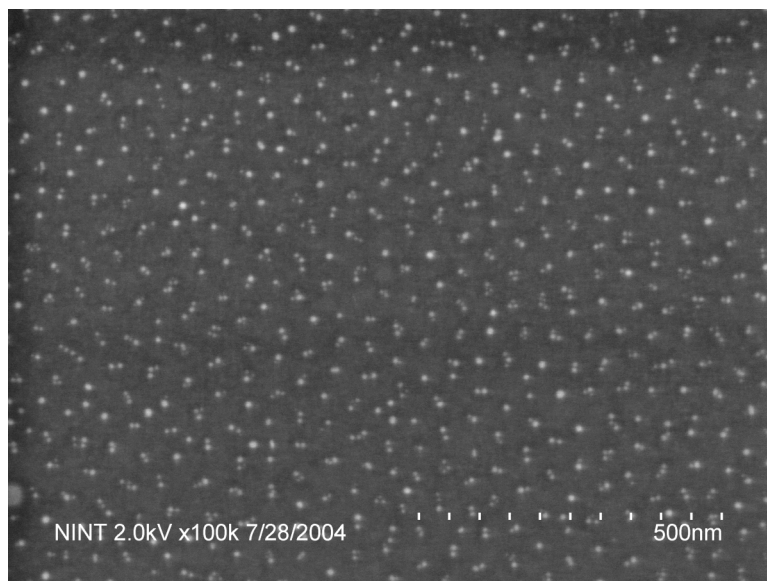
Deposition 2. For deposition method 2, 10 µl of the polymer solution was dropped on a 7 mm² wafer and spin coated at 2000 rpm for 1 min in an inert environment (same set-up as above). The samples were immersed in a mixture of 9 ml of 0.25-1% HF (aq), depending upon the substrate, and 1 ml 10⁻³ M AgNO₃ (aq) or HAuCl₄ (aq). The plating solution was not degassed prior to deposition and was carried out in ambient light. After immersion in the metal/HF solution, the samples were thoroughly rinsed with DI water and dried with nitrogen. The polymers were then removed in a toluene ultrasonic bath at 40-50°C for 5 min, and dried with nitrogen.

Characterization. The AFM used in this study was a Nanoscope IV (Digital Instruments/Veeco) using commercially available Si cantilevers. Images were acquired in the tapping mode. X-ray photoelectron spectroscopy (XPS) (Kratos Axis 165) was performed using a monochromatic Al Kα with a photon energy of 1486.6eV. The instrument was calibrated by the measurement of C1s. The Ag 3d and Au 4f metallic positions were also calibrated by sputtered Ag and Au films, respectively. SEM (Hitachi S-4880 FE-SEM) was generally performed using an electron energy of 10 keV.

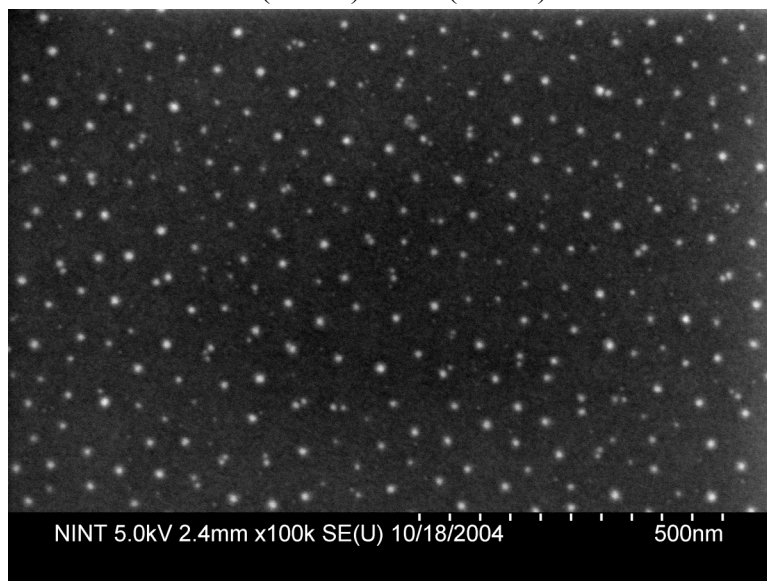
Figures

Figure SM1. SEM images of Ag on Ge(100) prepared by Ag^+ -PS(x)-P4VP(y) ($\text{Ag}^+/\text{4VP}=0.3$, Ag^+ ions preloaded).

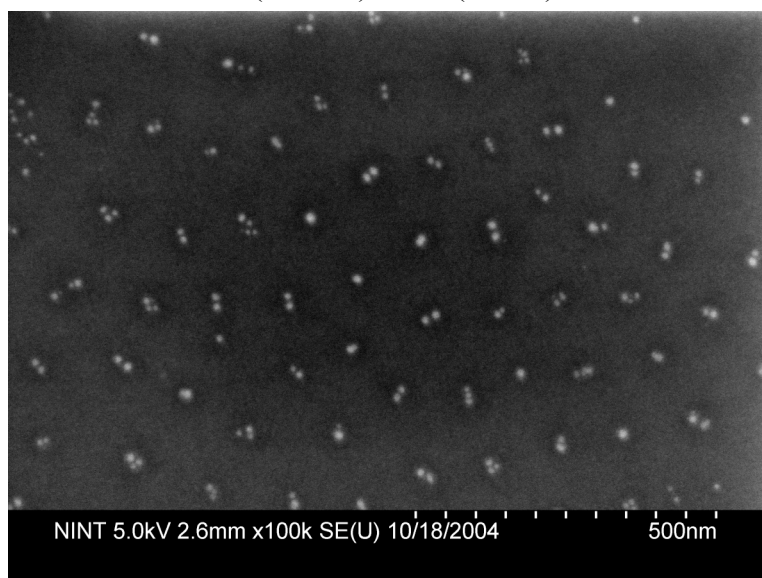
PS(20000)-P4VP(19000)



PS(57300)-P4VP(24700)



PS(128400)-P4VP(33700)

**Figure SM2. Ag 3d XPS of AgNO₃ deposition on Ge(100) and Si(100).**

- a) AgNO₃ dissolved within PS-P4VP (MW=20000-19000, ratio Ag⁺/4VP=0.3) in toluene and spin coated onto Si(100), native oxide capped.
- b) Removal of polymer with ultrasonication in toluene results in low Ag deposition.
- c) Same conditions as (a), except deposition on Ge(100), native oxide capped.
- d) Removal of polymer with ultrasonication in toluene results in strengthening of Ag signals due to exposure of Ag nanoparticles.

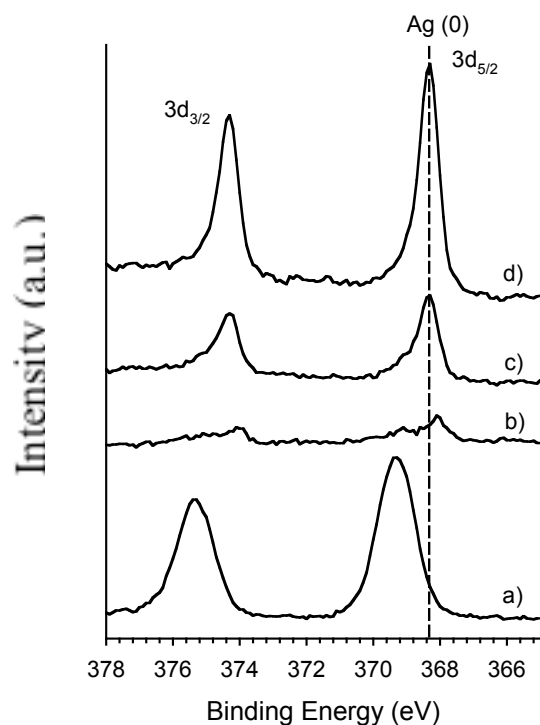


Figure SM3. Detailed AFM cross-section analysis of the silver nanoparticles on Ge(100) from Figure 1 of the main text.

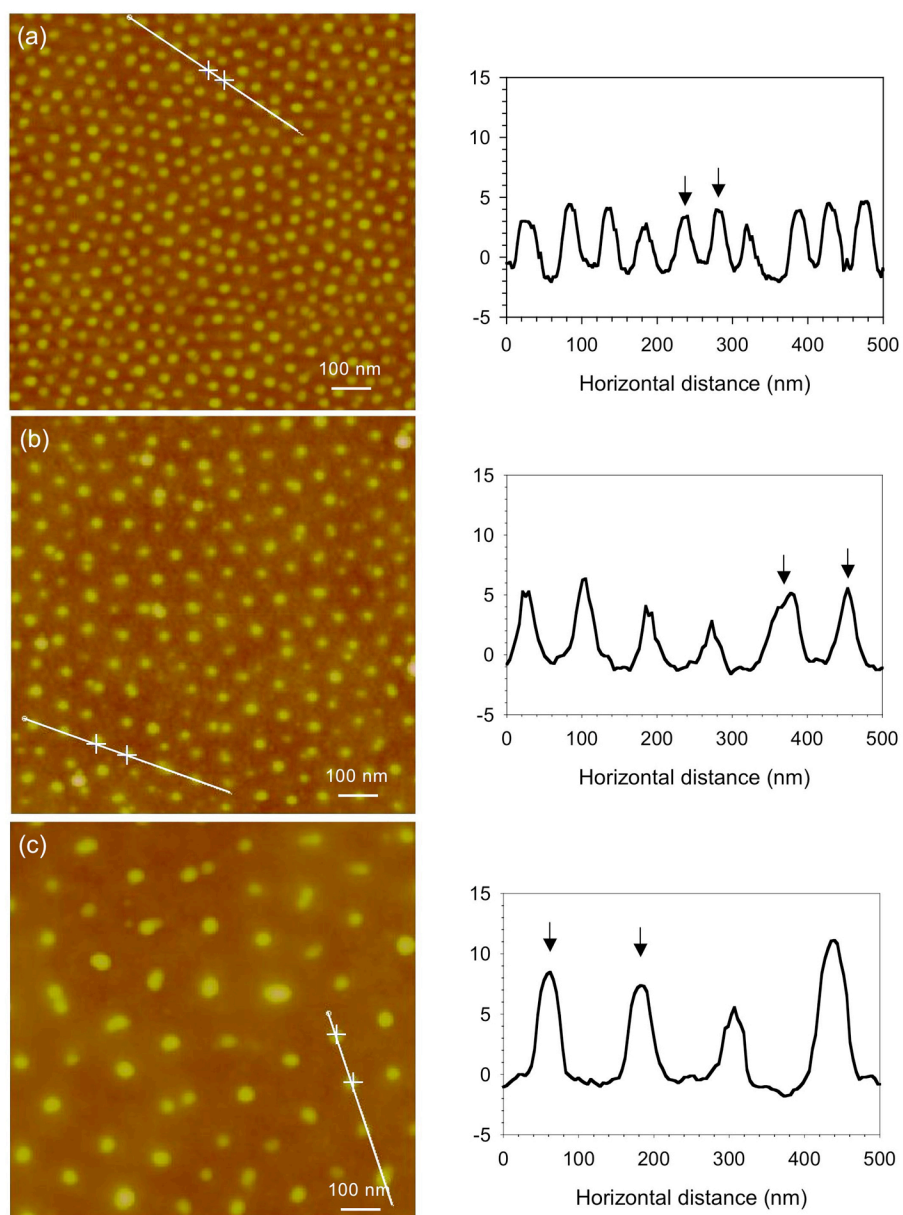


Figure SM4. SEM image of Ag on InP(100) prepared with an Ag⁺-PS(20000)-P4VP(19000)-loaded block copolymer (Ag⁺/4VP=0.3, Ag⁺ ions preloaded). (Deposition method 1-no HF exposure).

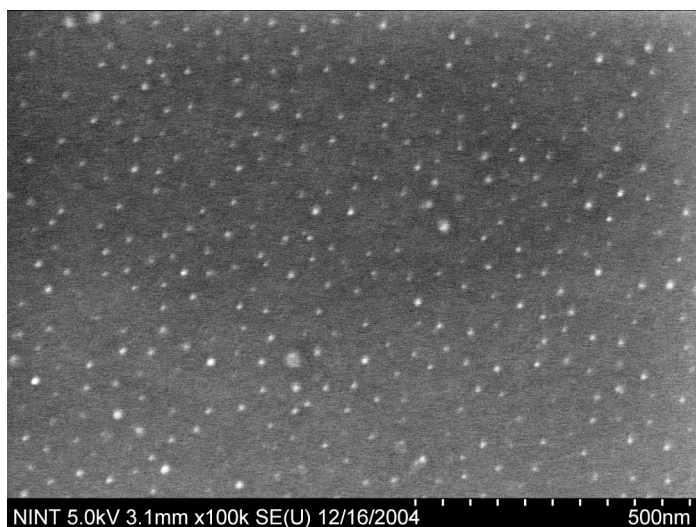


Figure SM5. Ag 3d XPS of AgNO₃ deposition on InP(100), native oxide-capped with no HF exposure (Deposition method 1).

a) AgNO₃ dissolved (preloaded) within PS-P4VP (MW=20000-19000, ratio Ag⁺/4VP=0.3) in toluene and spin coated onto InP(100).

b) Removal of polymer with ultrasonication in toluene results in strengthening of Ag signals due to exposure of Ag nanoparticles.

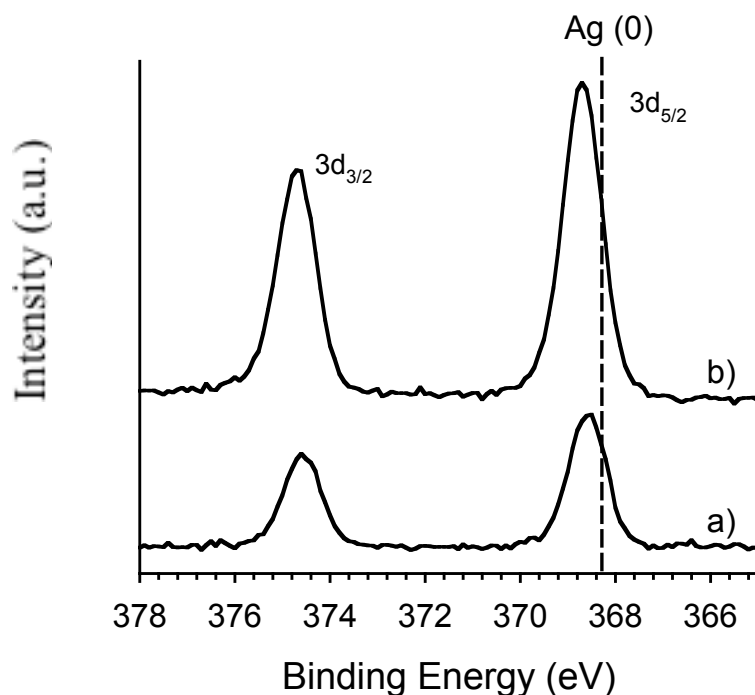


Figure SM6. Ag 3d XPS of AgNO₃ deposition on InP(100), native oxide-capped (Deposition method 2). PS-P4VP (MW=20000-19000) spin coated on InP (100) was immersed in 1 mM AgNO₃ and 1% HF for a) 30 s, b) 150 s, and c) 300 s. d)-f) Figures that correspond with a-c) showing XPS of samples following removal of polymer with ultrasonication in toluene; strengthening of Ag signals is due to exposure of Ag nanoparticles.

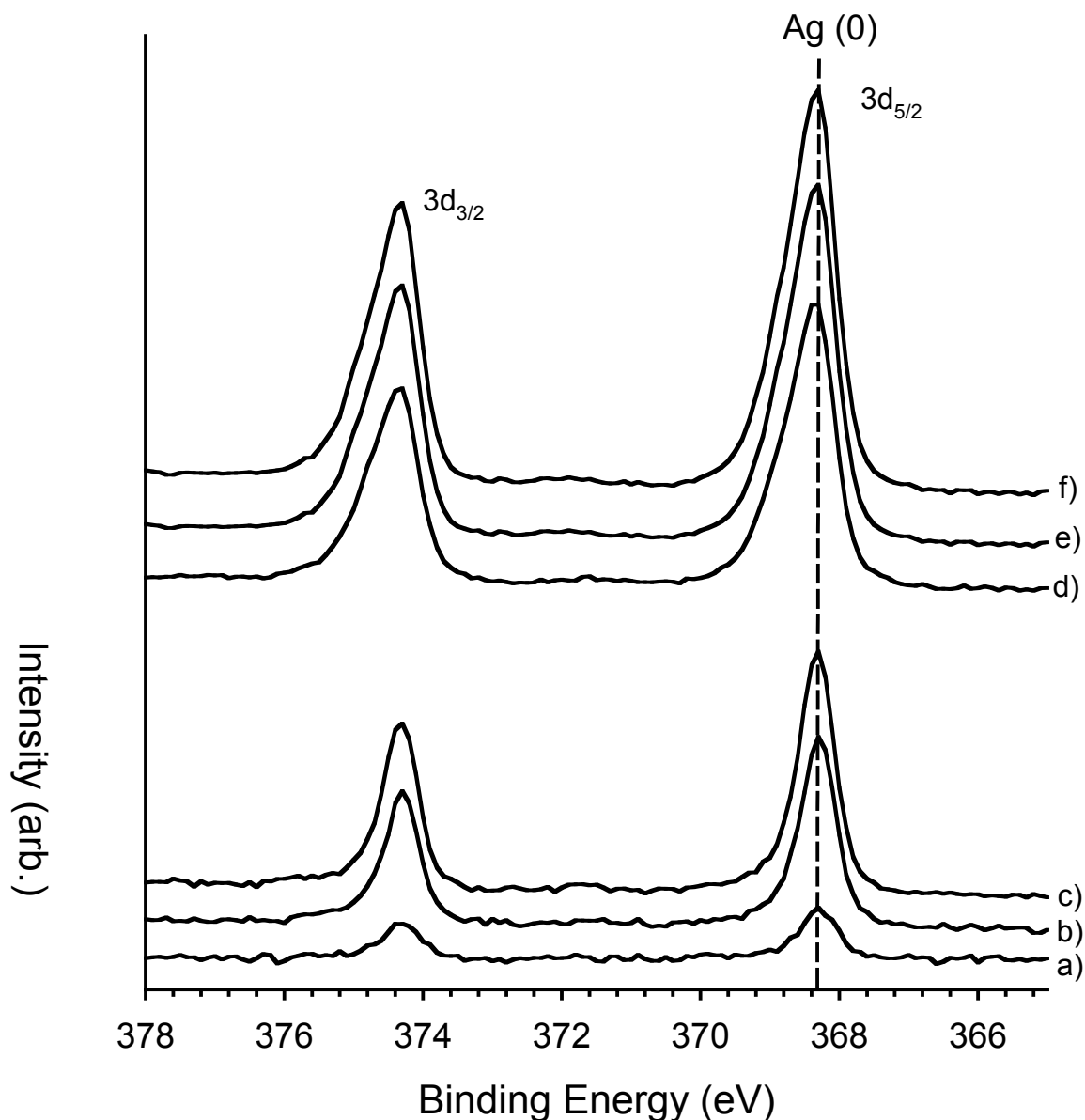
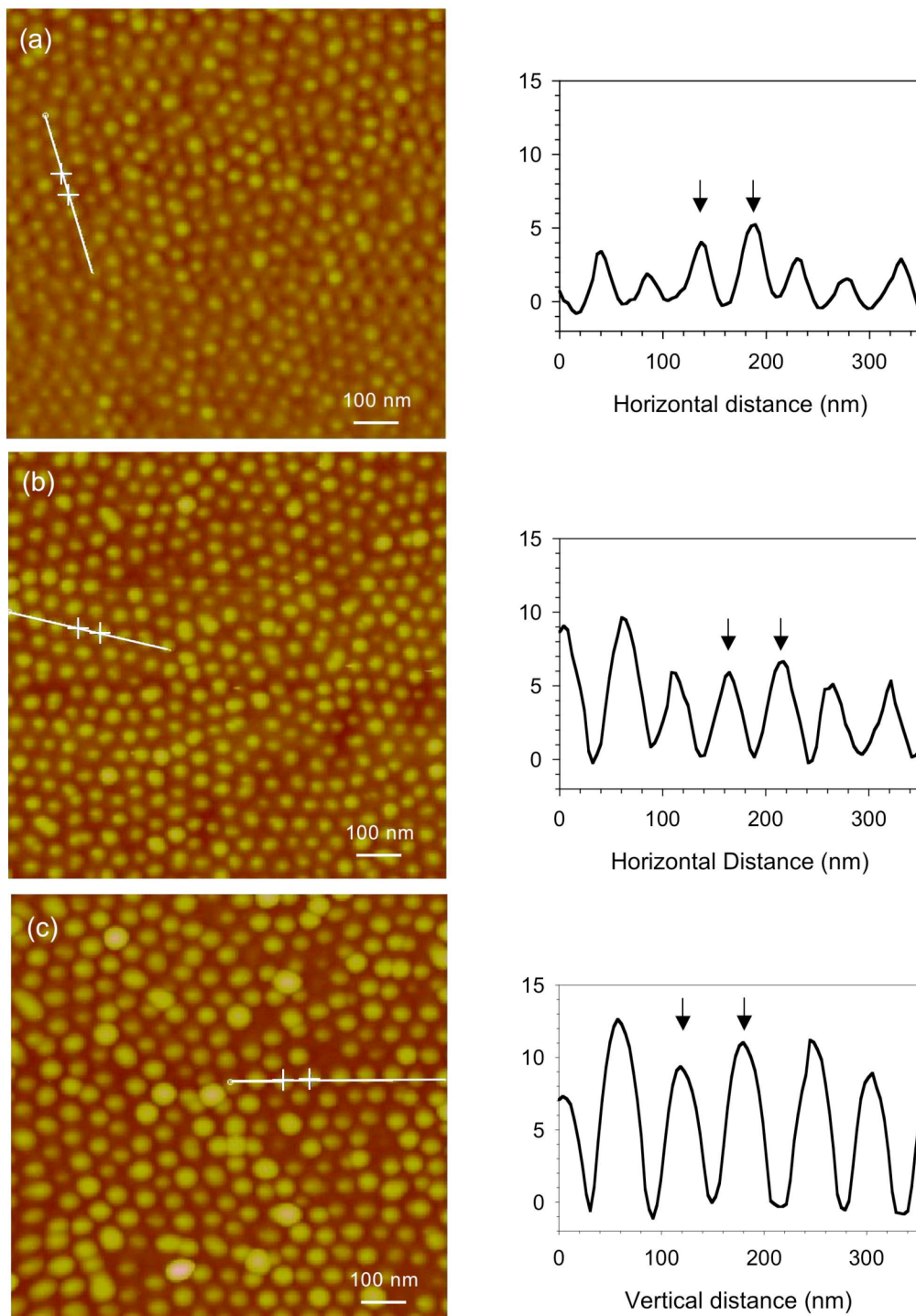
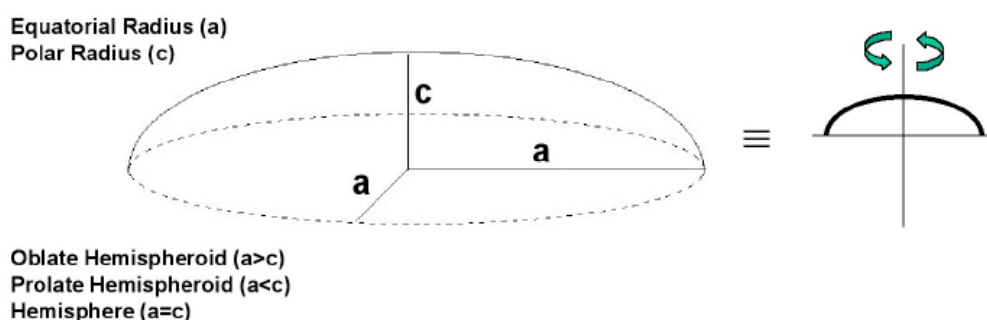


Figure SM7. Cross section AFM analysis of silver deposition of Ag on InP(100), corresponding to Figure 4 of the main text. Deposition in 1 mM AgNO₃/1% HF (aq) for: a) 30 s, b) 150 s, and c) 300 s.



Based on the cross sectional data for the Ag nanoparticles prepared on InP(100), the following data can be obtained. There is variability in the size and shape of each nanoparticle, and so these calculations are meant to provide a guiding approximation to nanoparticle size and number of atoms in each particle. As we have done previously, the shapes of the nanoparticles are assumed to be oblate hemispheroids; this figure is derived from the supplementary materials section of previous work by the Buriak group, published with reference 5. There are assumptions made here that render these calculations approximations: i) that the nanoparticles are perfect hemispheroids, although they may in fact penetrate below the visible surface of the InP(100) due to etching, and ii) that tip convolution effects in AFM are unimportant; to a first approximation, the diameters of nanoparticles measured by AFM compare well to those measured by SEM, although tip effects need to be investigated more thoroughly.



$$\text{Ellipticity } (e) \equiv [(a^2 - c^2)/a^2]^{1/2}$$

$$\text{Surface Area} = [2\pi a^2 + \pi(c^2/e)\ln[(1+e)/(1-e)]]/2$$

$$\text{Volume} = [(4/3)\pi a^2 c]/2$$

Summary

| Deposition Time (s) | Average diameter ¹ (nm) | Average height ¹ (nm) | Average volume ² (m ³) | Average weight ³ (g) | number of Ag nanoparticles (atoms) |
|---------------------|------------------------------------|----------------------------------|---|---------------------------------|------------------------------------|
| 30 | ~11 | ~3 | 1.9×10^{-25} | 2.0×10^{-18} | 1.1×10^4 |
| 150 | ~19 | ~6 | 1.1×10^{-24} | 1.2×10^{-17} | 6.6×10^4 |
| 300 | ~27 | ~11 | 4.2×10^{-24} | 4.4×10^{-17} | 2.46×10^5 |

Earlier literature for PS-P4VP block copolymers in toluene suggests an aggregation number *N* of ~6 for block copolymers with a molecular weight of PS₂₁₄₀₀-P4VP₂₀₇₀₀.⁶ The molecular weight utilized here is PS₂₀₀₀₀-P4VP₁₉₀₀₀ which is very similar. Assuming an *N* of 6, there are ~1085 pyridine groups per micelle. As can be seen from the table above, the number of Ag atoms/nanoparticle is substantially higher than 10³, suggesting that the block copolymer P4VP cores allow for free diffusion of Ag⁺ (aq) and/or swell with the Ag⁺ (aq) solution under these conditions.

Figure SM8. Au 4f XPS of HAuCl₄ deposition on GaAs(100), native oxide-capped (Deposition method 2).

a) PS-P4VP (MW=20000-19000) spin coated on GaAs (100) was immersed for 1 min in 1 mM HAuCl₄ and 1% HF (aq).

b) Removal of polymer with ultrasonication in toluene results in strengthening of Au signals due to exposure of Au nanoparticles.

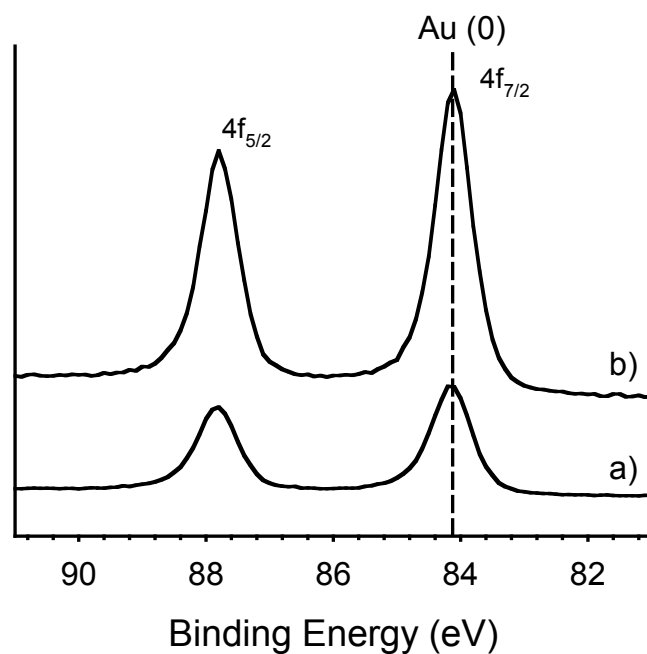
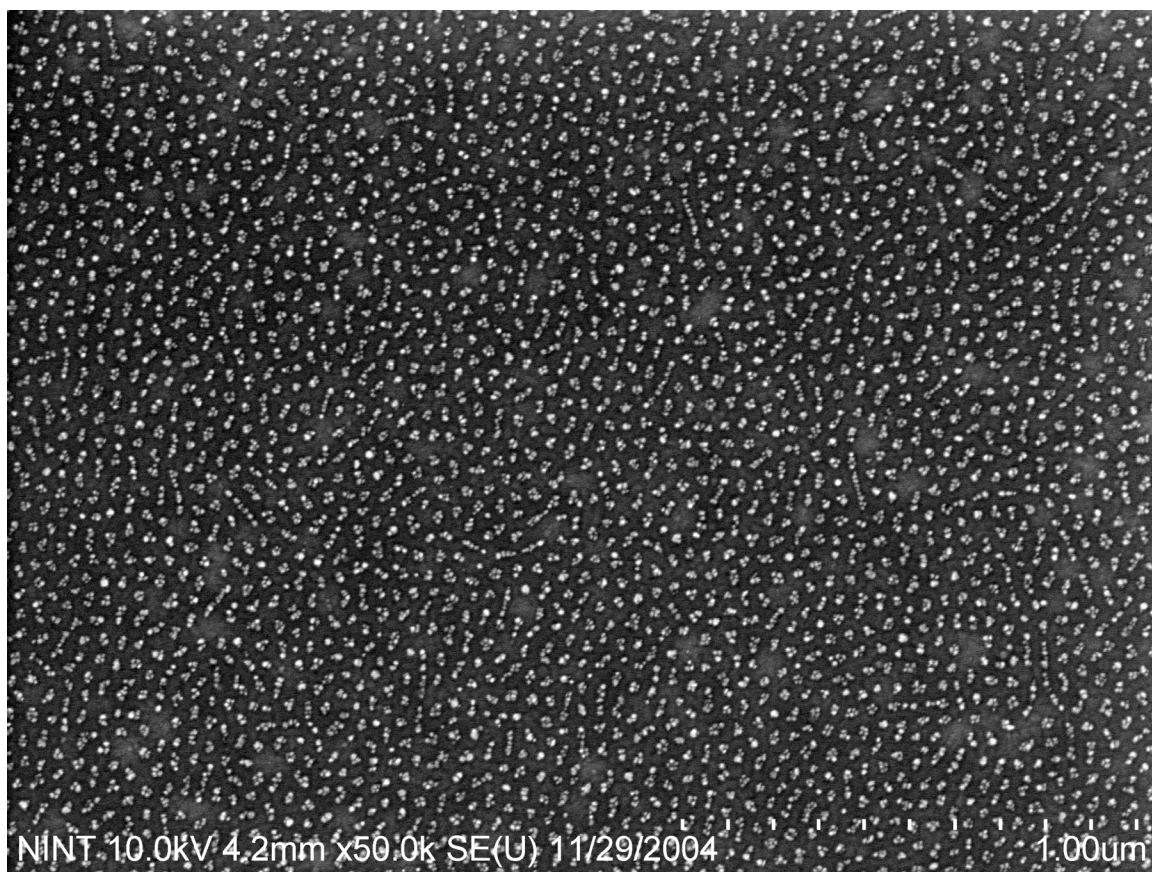


Figure SM9. Wide-view SEM of Au on GaAs(100) prepared by dipping PS(20000)-P4VP(19000) on GaAs into a mixture of 10^{-3} M HAuCl_4 (aq.) + 1% HF (aq) for 5 min.



References

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