SUPPORTING INFORMATION.

Controlled Electroless Deposition of Nanostructured Precious Metal Films on Germanium Surfaces

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Experimental Supplement

Materials. The following reagents were purchased from the indicated suppliers and used without modification: n-type (Sb-doped, 7 – 23 Ω·cm) and p-type (Ga-doped, 0.004 - 0.020 Ω·cm) crystalline germanium wafers (Waferworld, (100) orientation), intrinsic Ge chips (E. F. Fullam), 1-dodecanethiol (Aldrich, 98%), $HAuCl_4 \cdot 3H_2O$ (99.9%, Aldrich), $Na_2PdCl_4 \cdot 3H_2O$ (Pd, 99%, Strem), $Na_2PtCl_4 \cdot xH_2O$ (%Pt 42.65, Strem). Absolute ethanol was purchased from Pharmco Products Inc. Distilled water (18 MΩ) was purified using a Millipore (Barnstead) system. All other solvents and materials were obtained from commercial sources and used without modification.

General Procedure for Electroless Formation of Precious Metal Nanoparticles (Utilized for SEM, EDS, and XPS Experiments). Aqueous $AuCl_4^-$, $PdCl_4^{2-}$, and $PtCl_4^{2-}$ solutions were prepared by dissolving $HAuCl_4 \cdot 3H_2O$, $Na_2PdCl_4 \cdot 3H_2O$, $Na_2PtCl_4 \cdot xH_2O$, into deionized water (18 MΩ·cm), respectively. The Ge(100) substrates were cut into 0.5 × 0.5 cm rectangles and degreased by immersion into 4 successive baths of each of the following solvents: acetone, methanol, and deionized water. An additional soak in the above solvents was carried out with sonication for 2 min. The Ge(100) substrates were finally soaked in scintillation vials containing the aqueous metal salts for the designated time and temperature. The metal-deposited Ge substrate was then removed from the metal solution and washed with copious amounts of 18 MΩ water, ethanol, and pentane. The surface was subsequently blown dry with a stream of nitrogen.

Instrumentation

Atomic Force Microscopy (AFM). A scanning probe microscope (Nanoscope III, Digital Instruments) was utilized in tapping mode for imaging deposited nanocrystalline films. Noncontact Si (MikroMasch, NSC15/50) tips with a resonance frequency of ~340 KHz were employed with a scan rate of 1-4 µm/s.

Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). In order to perform structural and qualitative analysis, SEM and EDS were employed with a JEOL JSM-35 CF. Both were acquired utilizing an accelerating voltage of 35 kV.

X-Ray Photoelectron Spectroscopy (XPS). XPS spectra were measured using an Axis Ultra spectrometer (Kratos Analytical) with a monochromatic Al Kα source (225 W power). Survey (low-resolution) spectra were accumulated at a pass energy of 160 eV and were averaged from two scans with a step of 1000 meV. Adventitious hydrocarbon deposits from handling in air were used to reference all spectra at 284.0 eV.

FTIR Spectroscopy. FTIR analyses were conducted employing a Nicolet Nexus 670 spectrophotometer, operating in transmission mode with a DTGS detector. Spectra were recorded in 512 scans, with a spectral resolution of 4 cm^{-1}.

Thiol Chemisorption and Nanocrystallite Passivation with Self-Assembled Monolayers (SAMs)

Preparation of $C_{12}SH$ SAM on Nanostructured Au Deposited onto Ge(100). A degreased Ge(100) wafer fragment was immersed into an aqueous 2×10^{-3} M solution of $HAuCl_4$ for 30 min; the extended length of time leads to a thicker gold layer, allowing for FTIR visualization of the resulting alkanethiol monolayers. The gold-deposited Ge(100) substrate was then removed from the metal solution and washed with copious amounts of 18 MΩ water, ethanol, and pentane. The surface was blown dry with a stream of nitrogen and subsequently submerged into a 1×10^{-3} M solution of 1-dodecanethiol in ethanol for a period of 24 hours. Following removal of the sample from the thiol solution, it was thoroughly washed with ethanol and blown dry with nitrogen.

Additional Composition Characterization Data

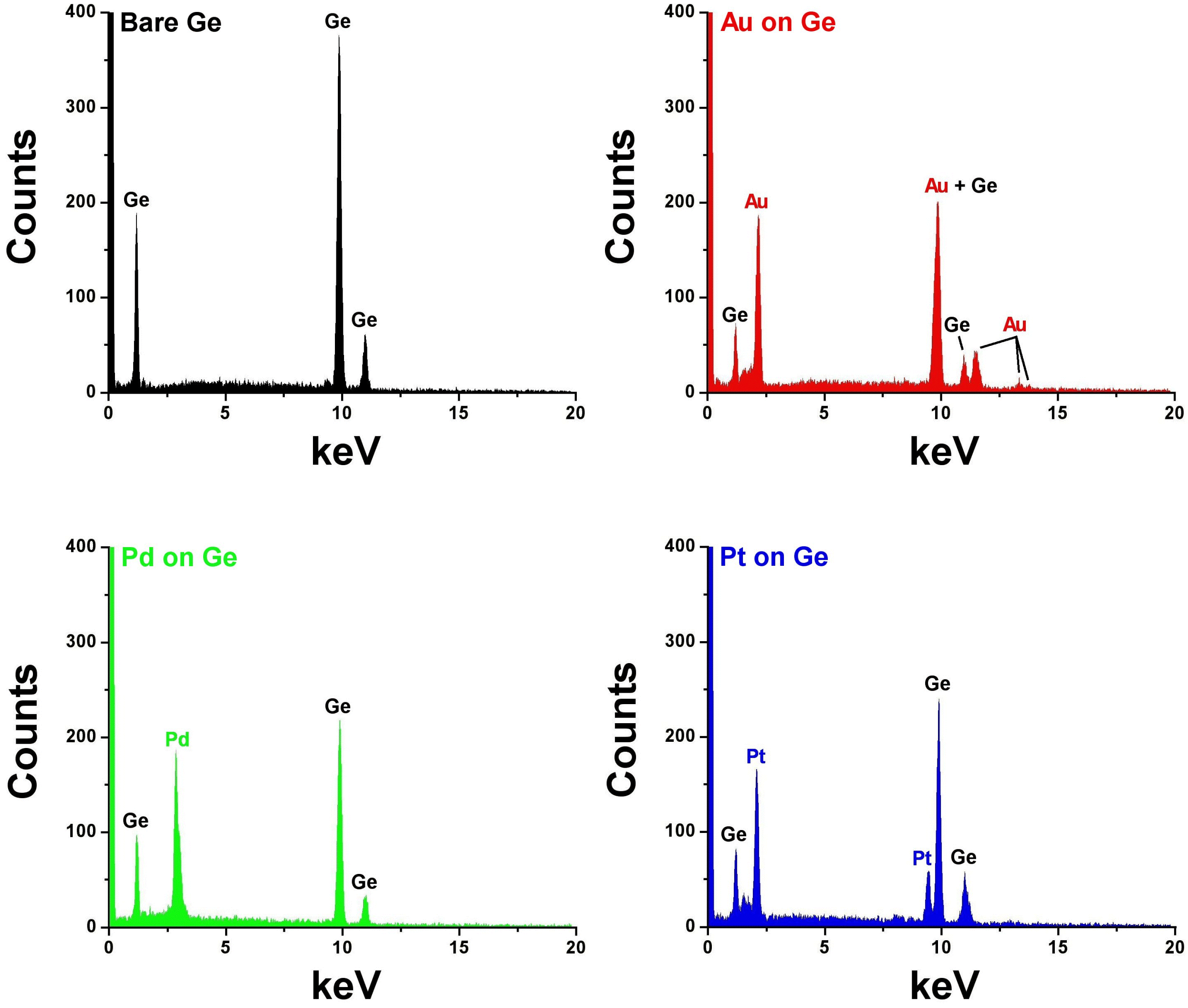


Figure SI-1. EDS spectra supporting metallic film growth on Ge(100); all samples were prepared through a 60 min immersion in a 1.0 mM solution of the corresponding metal salt.

Additional SEM Images

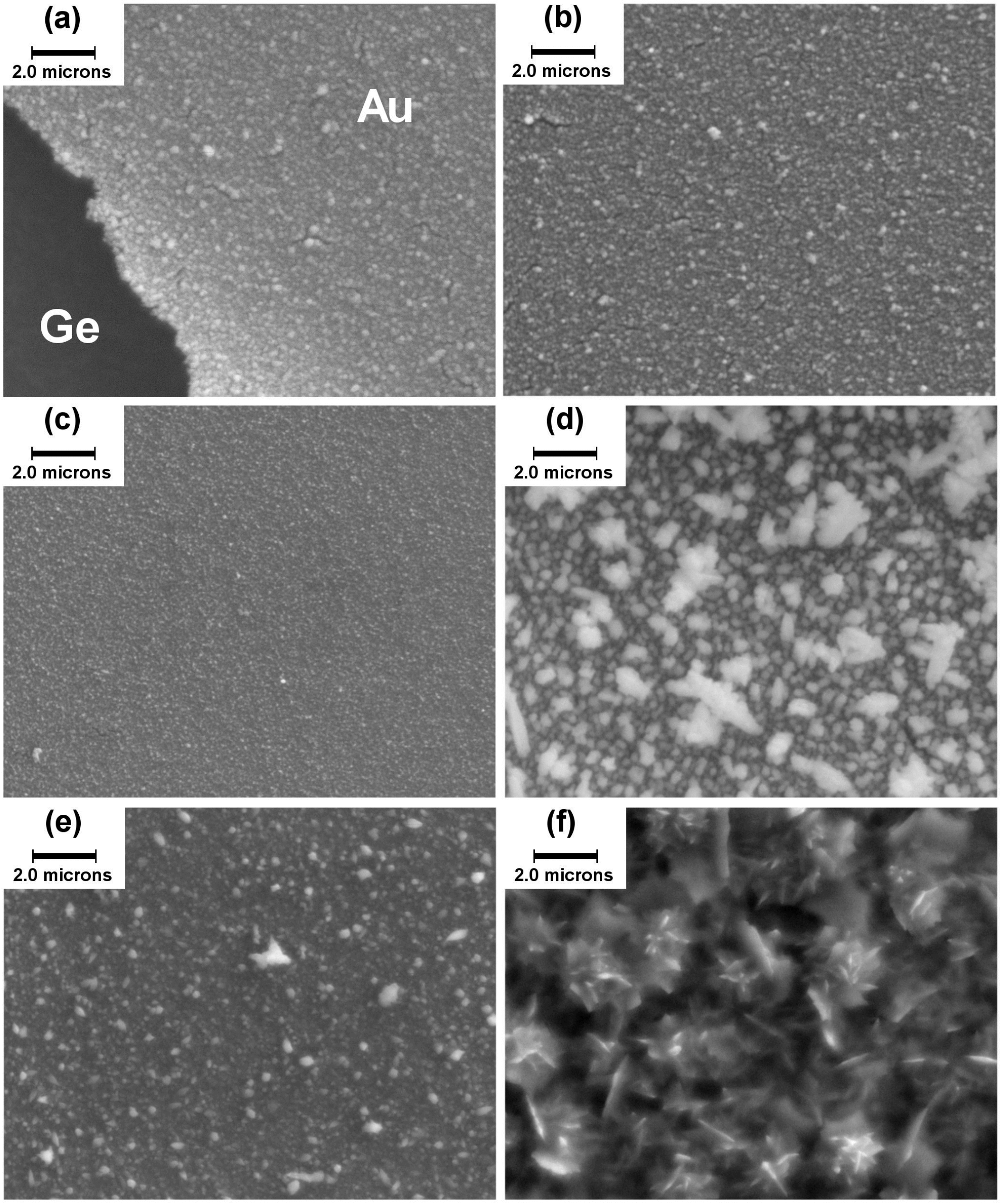


Figure SI-2. Scanning electron micrographs of Ge(100) immersed into 1.0 mM $AuCl_4^-$ for 90 min at (a,b) 25ºC; (c) 4ºC; (d) 70ºC; Ge immersed into (e) 10.0 mM and (f) 100.0 mM $AuCl_4^-$ for 10 min at 25ºC.

Additional AFM Images

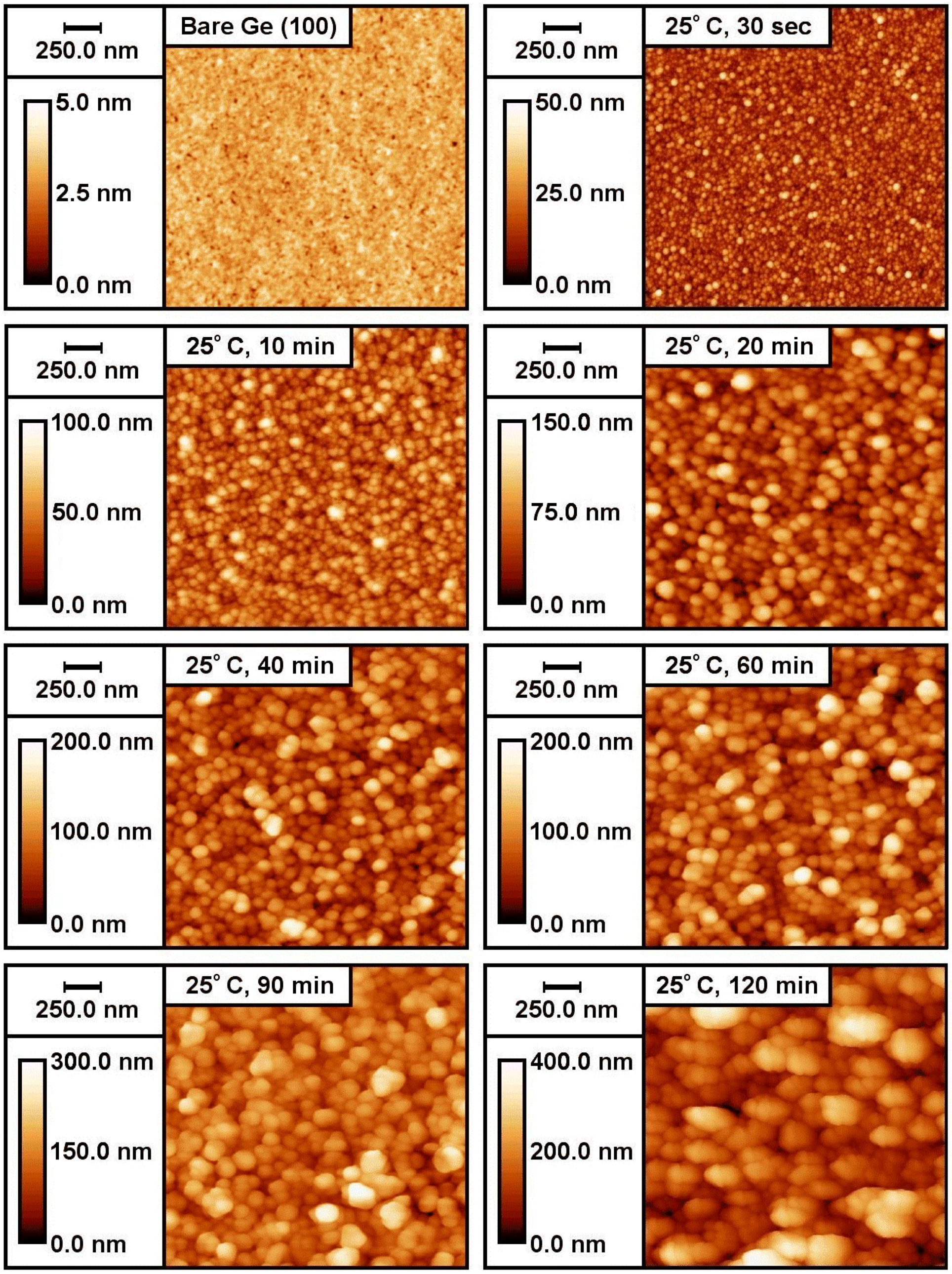


Figure SI-3. Tapping mode atomic force micrographs of Ge(100) immersed into 1.0 mM $AuCl_4^-$ at 25ºC for increasing immersion times (mean grain size increases from 31.0 ± 10.1 nm at 30 sec to 160.1 ± 57.2 nm at 120 min)

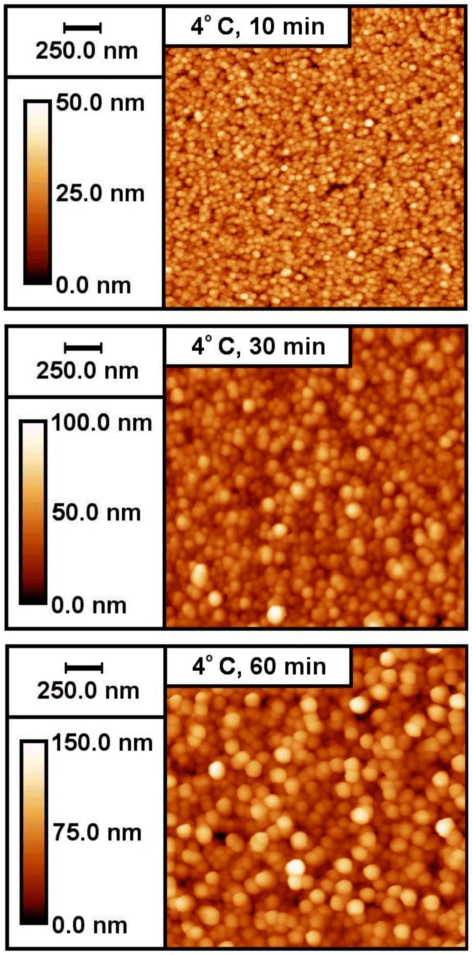


Figure SI-4. Tapping mode atomic force micrographs of Ge(100) immersed into 1.0 mM $AuCl_4^-$ at 4ºC for increasing immersion times

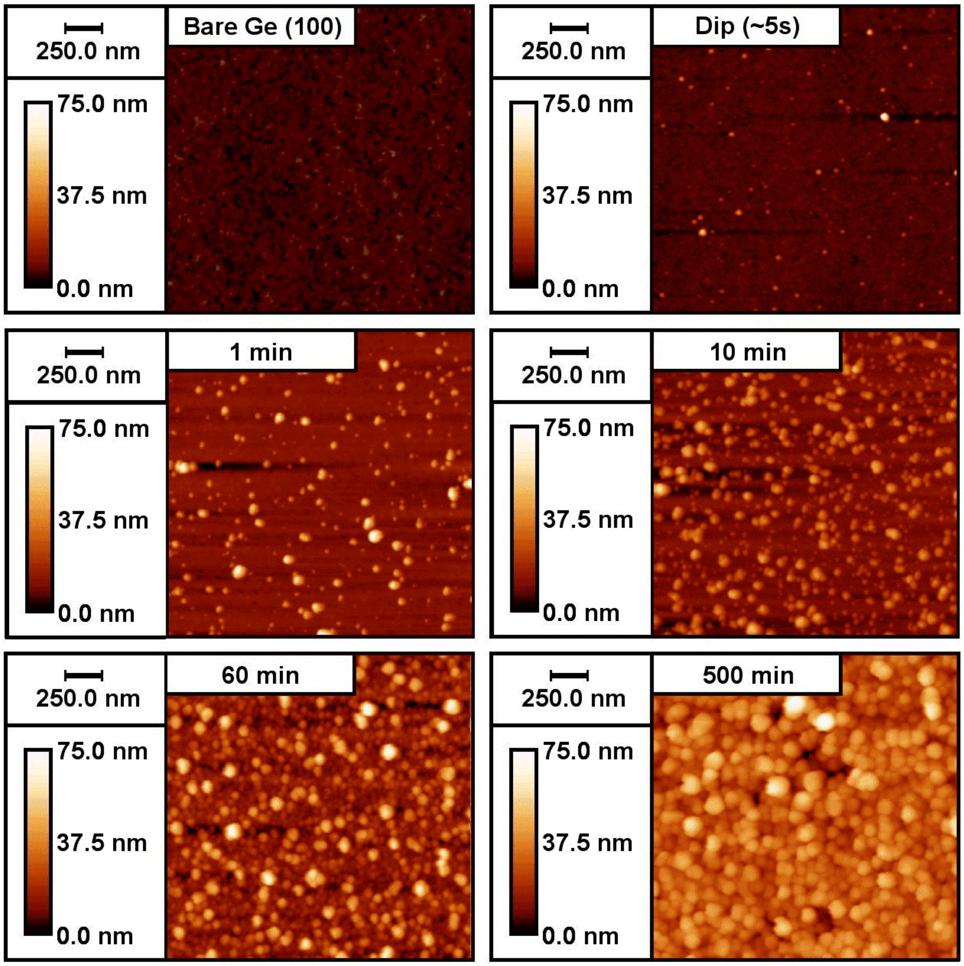


Figure SI-5. Tapping mode atomic force micrographs of Ge(100) immersed into 0.1 mM $AuCl_4^-$ at 25°C for increasing immersion times (These 2D micrographs correspond to their 3D representations, presented in Figure 5).

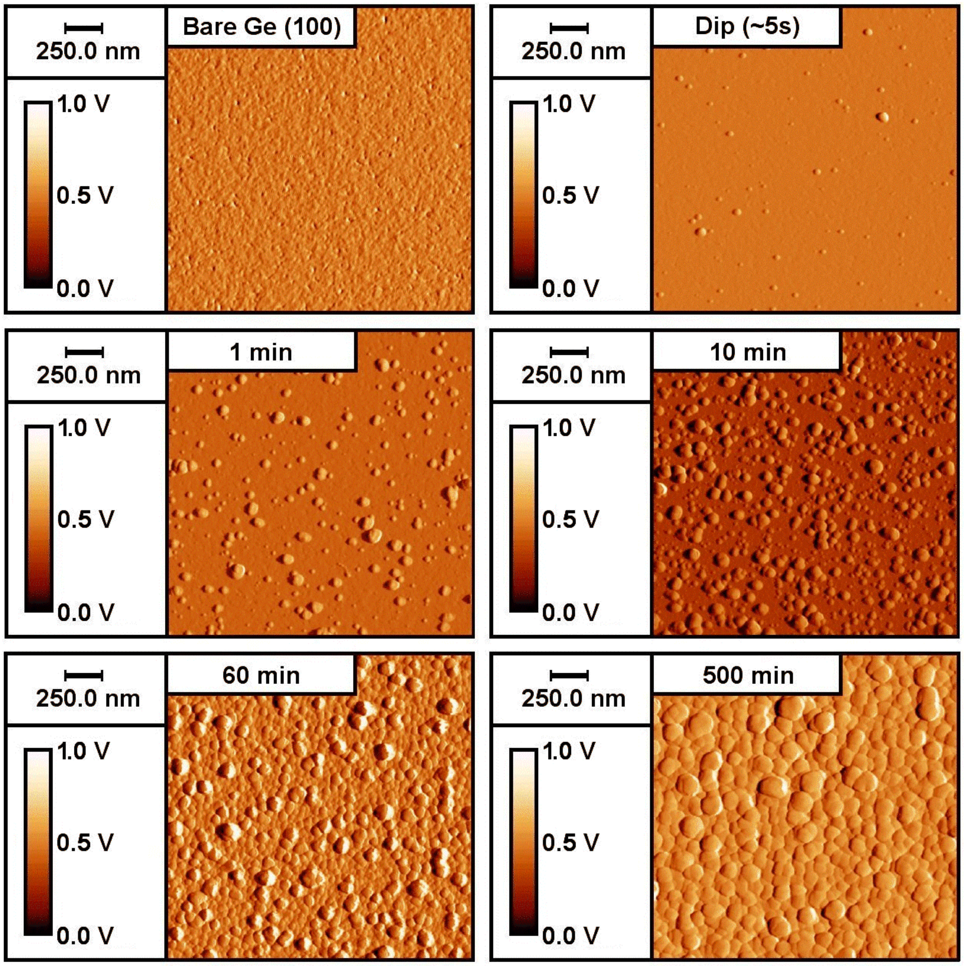


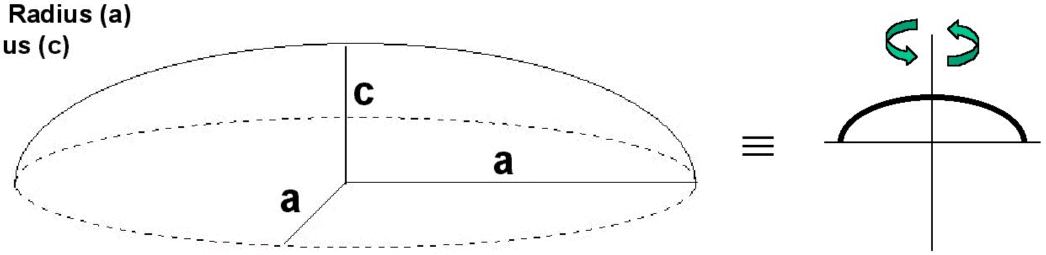
Figure SI-6. Tapping mode atomic force micrographs of Ge(100) immersed into 0.1 mM $AuCl_4^-$ at 25ºC for increasing immersion times (These amplitude images correspond to the height images, displayed in Figure SI-5)

Nanocrystallite Analysis of Au Nucleation Experiment

Oblate Hemispheroid:

The surface of revolution obtained by rotating a semiellipse about its minor axis

Equatorial Radius (a)
Polar Radius (c)



Oblate Hemispheroid (a>c)
Prolate Hemispheroid (a<c)
Hemisphere (a=c)

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

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

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

Figure SI-7. Oblate hemispheroid relationships utilized in data analysis

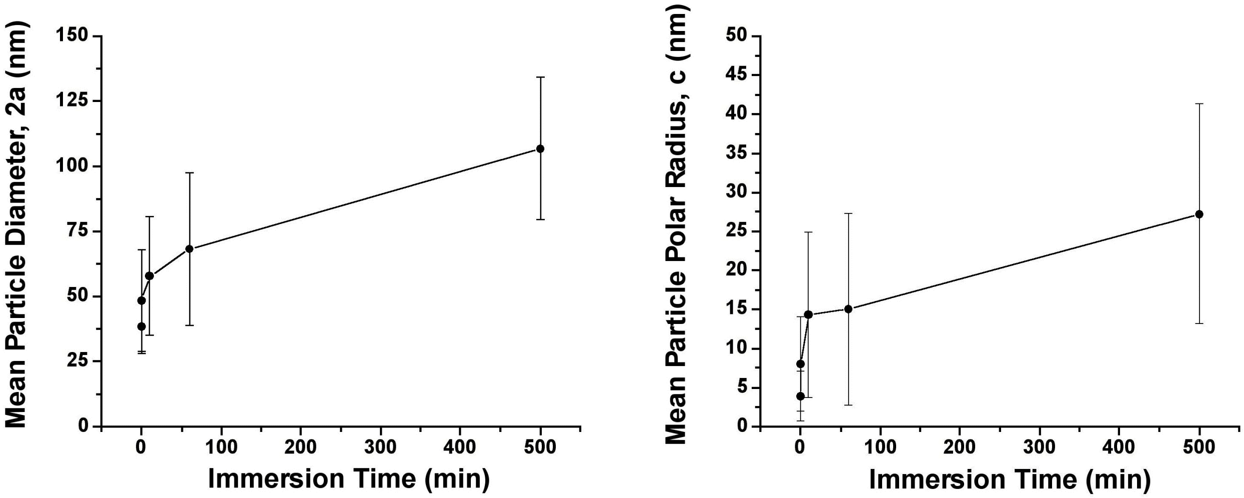


Figure SI-8. Mean nanoparticle diameter (2 x equatorial radius, a) and polar radius growth as a function of Ge(100) immersion time in 0.1 mM $AuCl_4^-$ at 25ºC

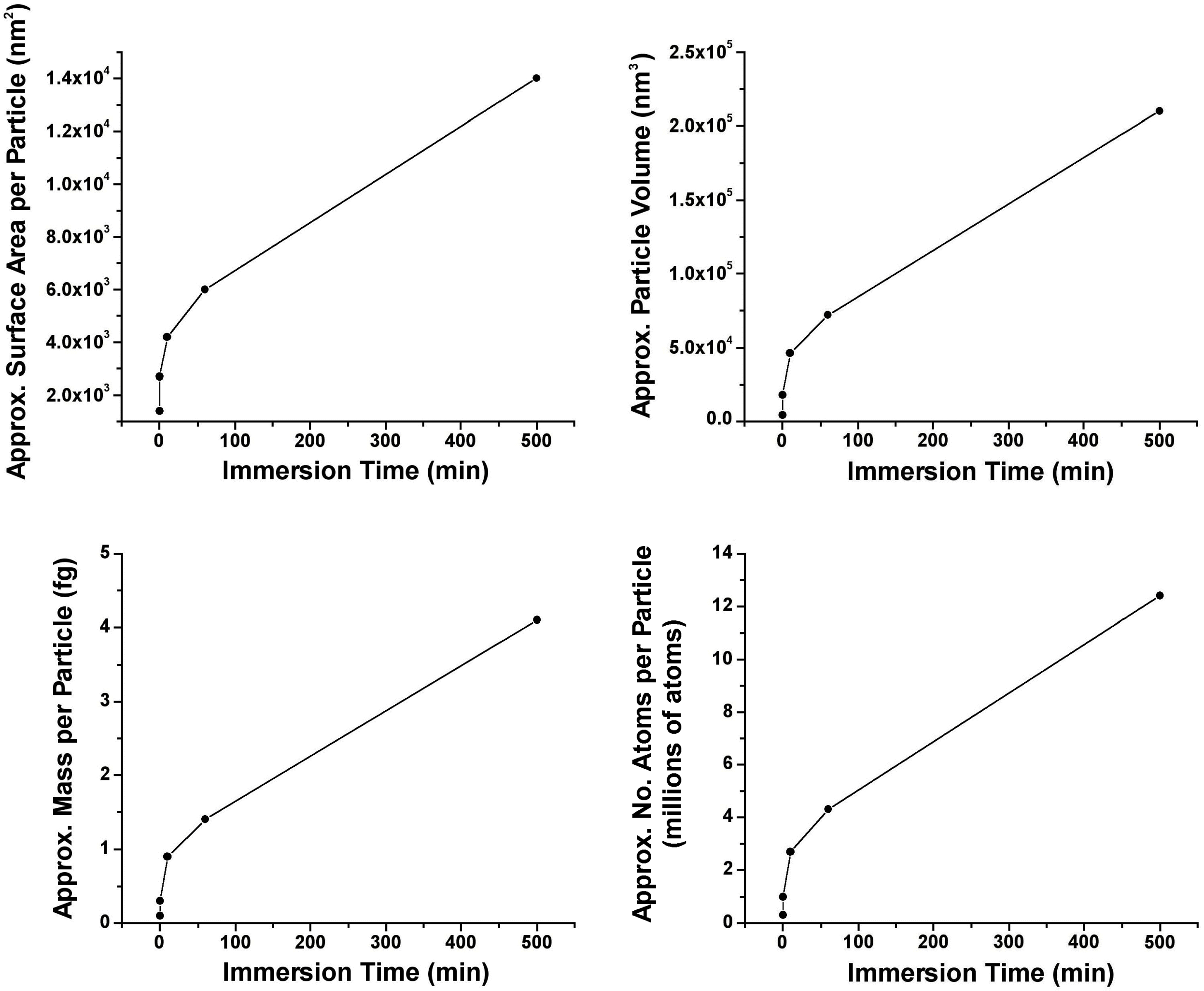


Figure SI-9. Approximate values of mean nanoparticle growth as a function of Ge(100) immersion time in 0.1 mM $AuCl_4^-$ at 25°C.