



Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2019

Synthesis and Properties of Au Hydride

Devika Sil⁺, Christopher Lane⁺, Ethan Glor⁺, Kyle D. Gilroy, Safiya Sylla, Bernardo Barbiellini, Robert Markiewicz, Maryam Hajfathalian, Svetlana Neretina, Arun Bansil, Zahra Fakhraai, and Eric Borguet*

Thin film preparation: The substrate-based gold nanostructures were produced using thermal dewetting^[1]. This process involves two steps: (i) sputter deposition [Gatan High Resolution Ion Beam Coater Model 681] of a gold thin film (typically ~10 nm) onto sodalime silica microscope glass slides with the resultant film being blue in color, and then (ii) heating from room temperature to 500°C for 15 min [Lindberg Blue M tube furnace, TF55035A-1] followed by cooling back to room temperature. All samples were heated in a constant flow of ultrahigh purity argon at 65 sccm. The assembled gold nanostructures have a hemispherical morphology^[1]. We used samples sputtered for 30s to obtain thin films.

Ellipsometry: *In situ* spectroscopic ellipsometry (M2000, J.A. Woolam) measurements were carried out to determine the dielectric constants of gold in presence and absence of H₂^[2]. The sample was housed in a cell [LinkamTHMS 600, Linkam Scientific Instruments] with quartz windows to let the incident broadband (400 nm < λ < 1600 nm) radiation in and out of the gas-controlled environment. The angle of incidence of the ellipsometric light was fixed at 70°. The dielectric function was obtained through fitting of the ellipsometric angles $\Psi(\lambda)$ and $\Delta(\lambda)$ which relate the ratio of reflection coefficient at two different polarizations of light, $\frac{r_P}{r_S} = \tan(\Psi) e^{i\Delta}$, to a thin-film model and forcing the fit to be Kramers-Kronig consistent. The dielectric constant of the film was modeled as a two-layer model. A Cauchy model with known coefficients for BK7 glass was used for the substrate layer. For the composite layer, all fits began with fitting the transparent region of the nanoparticle film (1000-1600 nm) to the Cauchy equation, $n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$, in order to characterize the thickness of the film, which was determined to be 8 nm. Fitting this region allows us to fit the thickness of the film independently of the extinction from the nanoparticles. Then, the fit was extended to lower wavelengths, where the material is absorbing through an isotropic wavelength-by-wavelength fit, which was set to be Kramers-

Kronig consistent. This brute force method fits an independent value for the complex dielectric constant at each wavelength. To reduce the number of independent variables and fit the optical constants of the film, the extinction of the nanoparticles was fit with an energy shift of $\epsilon_{\text{inf}} = 2.159$ using a series of three oscillators, the parameters for which are given in Table 1.

Table 1: Oscillator Parameters for the Fit in Figure 1

Oscillator Type	Amplitude	Breadth	Energy (eV)
Gaussian	3.321893	0.3631	2.182
Gaussian	1.093289	0.9038	2.418
Gaussian	1.997690	2.5722	3.975

All measurements were done at room temperature using identical flow rates of hydrogen and nitrogen. The plasmon resonance of the gold sample was excited from top, normal to the sample surface with a broadband visible excitation. Figure 2b schematically shows the experimental setup with nanoparticle films under N_2 gas and the ellipsometry beams set at an angle of incidence of 70° .

DFT Calculations: We have performed DFT calculations using the pseudopotential projected augmented wave method^[3] implemented in the Vienna *ab initio* simulation package (VASP)^[4-6] with an energy cutoff of 350 eV for the plane-wave basis set. The exchange-correlation functional was treated using the generalized gradient approximation (GGA)^[7]. A $7 \times 7 \times 1$ Monkhorst-Pack k-point mesh was used for momentum integrations. All sites in the unit cell along with the unit cell dimensions were relaxed using the conjugate gradient algorithm to minimize energy with an atomic force tolerance of 0.01 eV/\AA . The top site was not considered because when we relaxed the system with H at the top site, H moved to the HCP or FCC site in agreement with Ferrin *et al.* where the FCC site was found to be the most stable.^[8] Moreover, our results without dipole corrections are in good agreement with other accurate calculations given in

Refs. [8–11], thus we thus conclude that the correction can be neglected in the present case. The Friedel oscillation in gold is on a distance $2\pi/2k_F = 2.8$ Å that can be easily accommodated in our 8.66 Å x 8.66 Å unit cell. The vacuum layer of 18 Å is designed to prevent spurious interaction of H atoms in the image cell. The optical properties were calculated following the method described by Gajdoš *et al.* ^[12] All of our theoretical data is publically available in the NOMAD database so that the reproducibility of our work can be checked.^[13]

References:

- [1] C. V. Thompson, *Annual Review of Materials Research* **2012**, *42*, 399–434.
- [2] D. Sil, *Synthesis and Applications of Plasmonic Nanostructures*, Temple University, **2015**.
- [3] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758–1775.
- [4] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *48*, 13115–13118.
- [5] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169–11186.
- [6] G. Kresse, J. Furthmüller, *Computational Materials Science* **1996**, *6*, 15–50.
- [7] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [8] P. Ferrin, S. Kandoi, A. U. Nilekar, M. Mavrikakis, *Surface Science* **2012**, *606*, 679–689.
- [9] S. Takagi, J. Hoshino, H. Tomono, K. Tsumuraya, *J. Phys. Soc. Jpn.* **2008**, *77*, 054705.
- [10] S.-W. Wang, W. H. Weinberg, *Surface Science* **1978**, *77*, 14–28.
- [11] G. Kresse, J. Hafner, *Surface Science* **2000**, *459*, 287–302.
- [12] M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller, F. Bechstedt, *Phys. Rev. B* **2006**, *73*, 045112.
- [13] **2018**, DOI <http://dx.doi.org/10.17172/NOMAD/2019.02.25-1>.