

Electrochemical restructuring of plasmonic metamaterials

M. Ruther,^{1,2,3,a)} L.-H. Shao,^{1,2,4} S. Linden,^{1,2,3,5} J. Weissmüller,^{1,2,4} and M. Wegener^{1,2,3}

¹*Institut für Nanotechnologie, Karlsruhe Institute of Technology (KIT), D-76021 Karlsruhe, Germany*

²*DFG-Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany*

³*Institut für Angewandte Physik, Karlsruhe Institute of Technology (KIT), D-76128 Karlsruhe, Germany*

⁴*Institute of Materials Physics, Hamburg University of Technology, Eissendorfer Straße 42, D-21073 Hamburg, Germany*

⁵*Physikalisches Institut, Universität Bonn, Nußallee 12, D-53115 Bonn, Germany*

(Received 3 November 2010; accepted 13 December 2010; published online 7 January 2011)

Recent electrochemical experiments on gold-based photonic metamaterials have shown reversible optical modulation as well as an irreversible reduction in the plasmonic damping. Here, we systematically study the latter aspect as a possible means of postprocessing plasmonic gold nanoantennae arrays aiming at loss reduction. We characterize the samples by optical spectroscopy, electron microscopy, and atomic-force microscopy. For sub-10 nm gold thicknesses, the measured damping decreases by factors exceeding 3; for 20–30 nm thin structures, the obtained loss reduction still amounts to about 30%. © 2011 American Institute of Physics. [doi:10.1063/1.3533807]

In the fields of plasmonics and metallic photonic metamaterials, reduction in losses is of obvious and utmost importance. Two main routes have been followed: (i) active loss reduction by introducing gain (for recent experimental examples, see Refs. 1–3) and (ii) passive loss reduction by improving the metal quality. Regarding (ii), published experimental work comprises studies on metal alloys⁴ and post-tempering of metal nanostructures.⁵ Another route, electrochemical processing, has been investigated on single gold nanoparticles and on extended metal electrodes.^{6,7} Electrochemical postprocessing has recently also appeared as a side aspect in electrochemical modulation experiments on gold split-ring resonator arrays.⁸ In this letter, we systematically investigate this aspect in terms of a postprocessing procedure that reduces the plasmonic losses under ambient conditions after electrochemical processing compared to before. Arrays composed of rectangular gold pads (antennae) serve as an example. We observe huge effects for film thicknesses near the percolation threshold and significant effects for typical gold-film thicknesses on the order of 20–30 nm. Any such postprocessing is mainly expected to reduce excessive Ohmic (or nonradiative) damping. Small effects on the radiative damping may arise though due to changes in the metal-nanostructure shape. Ideally, after postprocessing, one is left with the intrinsic radiative damping only.

The gold nanoantennae arrays in this letter have been fabricated using standard electron-beam lithography on glass substrates coated with a 10 nm thin film of indium tin oxide (ITO). As usual, the ITO film is crucial to avoid charging effects in the fabrication process. More importantly, the ITO combined with the nanoantennae arrays serves as the working electrode in our electrochemical experiments. In addition, we use a nominally 2 nm thin layer of Cr as an adhesion promoter. All materials are deposited by standard high-vacuum electron-beam evaporation. Gold has been deposited at a rate of 0.1 nm/s. All quoted thicknesses have been mea-

sured by atomic-force microscopy (AFM). Each nanoantennae array has a footprint of $80 \times 80 \mu\text{m}^2$. Our electrochemical experiments have been performed in a quartz glass cuvette filled with a 0.7M solution of NaF (Suprapur, Merck, Germany) in ultrapure 18.2 M Ω cm grade water (Arium 611, Sartorius, Germany) and open to air. All sample and electrode cleaning procedures are analogous to those in Ref. 9. The sample is immersed in the solution and its potential is measured relative to a standard reference electrode, Ag/AgCl in saturated KCl solution, which is controlled by a commercial potentiostat (VoltaLab PST 050, Radiometer Analytical, France). A macroscopic gold spiral serves as the counter electrode in our setup. For the restructuring procedure, the applied electrode potential has been varied between -0.9 and $+1.0$ V for 30 complete cycles. This potential window includes the reversible adsorption/desorption of about one monolayer of oxygen on the gold surface.

To monitor the process *in situ*, we measure the normal-incidence transmittance spectra as described previously.⁸ The extinction spectra are the negative logarithm of the measured transmittance. All these spectra (see Ref. 8 or right column of Fig. 2) can nicely be fitted by Lorentzians. The resulting fit parameters (during cycling within the electrolyte), i.e., the damping and the resonance center frequency, are depicted in Fig. 1. Clearly, the damping gradually decreases and the center frequency gradually shifts toward the blue. This effect can be phenomenologically explained by a decrease in the resistance and capacitance of the gold nanostructures due to surface restructuring. Superimposed on these trends, we again find electrochemical modulation of the transmittance within each cycle, as previously discussed in Ref. 8. In terms of an electrochemical postprocessing procedure, the comparison of the corresponding extinction spectra in air (rather than in the electrolyte) before and after the complete cycling is more relevant. Corresponding data are exhibited in the right column of Fig. 2 for the two orthogonal linear incident polarizations of light and for five different gold-film thicknesses (a)–(e). In each of these cases, we find a substantial sharpening of the plasmonic resonances. As expected for any

^{a)}Author to whom correspondence should be addressed. Electronic mail: matthias.ruther@kit.edu.

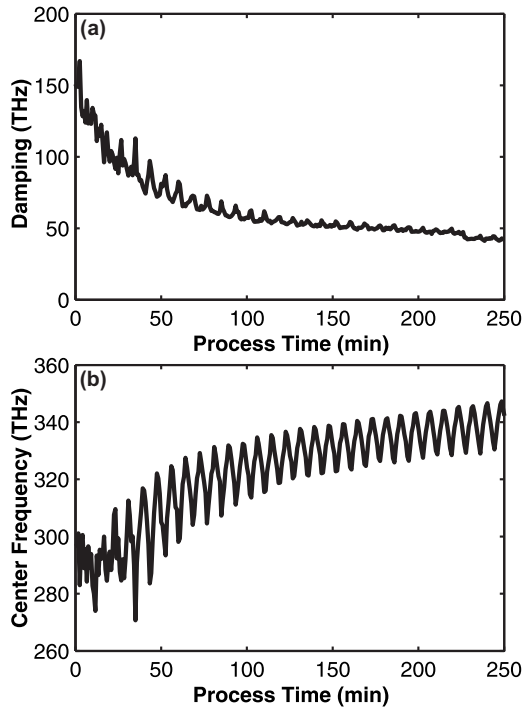


FIG. 1. (a) Plasmonic damping and (b) resonance center frequency vs time as derived from Lorentzian fits to the measured extinction spectra taken under normal incidence with horizontal polarized light inside the electrolyte during periodic electrochemical cycling in the potential window from -0.9 to $+1.0$ V and a cycling time of about 8 min/cycle. Note the beneficial reduction in damping (i.e., losses) vs time. The sample in this example is an array of gold pads with dimensions 145×95 nm², a lattice constant of 300 nm, and an average gold-film thickness of 7.9 nm.

harmonic-oscillator resonance, this sharpening due to loss reduction is accompanied by an increase in the extinction peak height.

It is interesting to ask whether these beneficial optical trends are accompanied by signatures in the electron micrographs and/or AFMs before (left column of Fig. 2) and after (center column) the complete electrochemical cycling. To allow for a direct comparison and to obtain good image contrast, we have adjusted the gray levels in the electron micrographs such that the substrate on average appears black, whereas the gold antennae on average appear white. The resulting effects in Fig. 2 are most pronounced for thin “films” near or even below the percolation threshold. For example, for a nominal gold-film thickness of 7.1 nm, the disconnected islands of gold “before” cycling develop into a film “after” the cycling. This trend is also accompanied by a slight reduction in the lateral extent of the metal pads. In contrast, the gold thickness as observed in the AFM data hardly changes between before and after. To emphasize this aspect, we show an AFM line scan through the center of the pad in each case. Note that the films after cycling appear much smoother in the scanning electron microscopy images. The AFM tip is obviously not able to reach into the steep valleys seen in the electron micrographs (because of its large opening angle). It has been reported that transient roughening, accompanied by an increase in surface diffusivity, accompanies the oxidation/reduction treatment of noble metal electrodes.^{10,11} In our experiments, the “smoothing” also only happened when we included an oxidation/reduction potential window, and from the Lippmann equation it is known that in this potential window the gold-electrolyte surface ten-

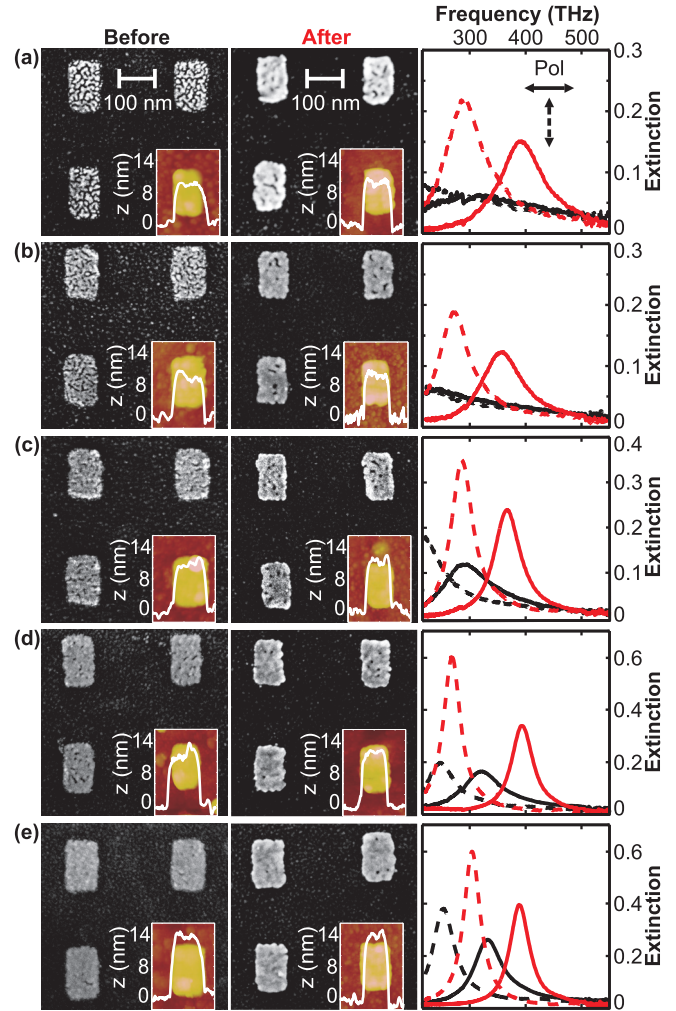


FIG. 2. (Color) Gold nanoantennae arrays of different average gold-film thicknesses [increasing from (a) to (e) with 7.1, 7.9, 8.6, 9.8, and 11.5 nm] before and after electrochemical cycling (see Fig. 1). All data are taken under ambient conditions, i.e., outside of the electrolyte. The left column exhibits scanning electron micrographs before cycling as well as AFM data on one antenna with an AFM line scan profile. The center column depicts corresponding data after cycling. Note the distinct changes in the spectra that are especially pronounced for thin gold structures. The right column reveals corresponding measured normal-incidence extinction spectra before (black curves) and after (red curves) cycling for vertical (dashed) and horizontal (solid) incident linear polarizations of light.

sion is reduced.¹² The reduction in the surface tension of the gold-electrolyte interface favors wetting of the substrate by gold and, therefore, a smoother surface. We conclude that the change in the optical properties is accompanied by a clear restructuring of the gold atoms within the antennae that is most pronounced for very thin films.

To give an overview on the results of our postprocessing study, Fig. 3 summarizes the deduced damping values before and after the electrochemical cycling for all samples shown in Fig. 2 as well as for several others, especially others with yet much larger gold-film thicknesses for which we find only insignificant changes in the electron micrographs (not depicted). Obviously, the damping reduction decreases with increasing gold thickness. This trend is expected as one easily gets closed thick films by evaporation. Note, however, that we still get a damping reduction as large as 30% even for 20–30 nm thick gold films. Such films are quite typical for photonic metamaterials.¹³ Yet much larger improvements can

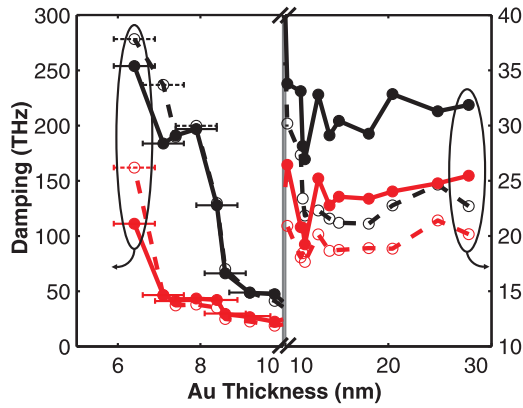


FIG. 3. (Color) Plasmonic damping as derived from Lorentzian fits to measured extinction spectra like the ones shown in Fig. 2 before (black curves) and after (red curves) electrochemical cycling vs the average gold-film thickness given in two different ranges: 6–10 nm in (a) and 10–30 nm in (b). The full symbols and solid lines correspond to horizontal linear polarization of the incident light, whereas the open symbols with dashed lines to vertical polarization.

be reached for gold films below 10 nm thickness.

In conclusion, we have presented electrochemical cycling as an interesting means of postprocessing metallic photonic metamaterial samples. This approach aiming at loss reduction in plasmonic resonances is complementary to the recently discussed thermal annealing of photonic metamaterials⁵ in that the electrochemical cycling is advantageous if applied to very thin gold films.

We thank Michael Engel and Markus Moosmann for experimental assistance in the AFM measurements. We acknowledge financial support through CFN subprojects A 1.2, A 1.5, and A 1.6. The project PHOME is supported by the European Commission under FET-Open Grant No. 213390. The project METAMAT is supported by the Bundesministerium für Bildung und Forschung (BMBF). The Ph.D. education of M.R. is embedded in the Karlsruhe School of Optics and Photonics (KSOP).

- ¹E. Plum, V. A. Fedotov, P. Kuo, D. P. Tsai, and N. I. Zheludev, *Opt. Express* **17**, 8548 (2009).
- ²S. Xiao, V. P. Drachev, A. V. Kildishev, X. Ni, U. K. Chettiar, H.-K. Yuan, and V. M. Shalaev, *Nature (London)* **466**, 735 (2010).
- ³N. Meinzer, M. Ruther, S. Linden, C. M. Soukoulis, G. Khitrova, J. Hendrickson, J. D. Olitsky, H. M. Gibbs, and M. Wegener, *Opt. Express* **18**, 24140 (2010).
- ⁴D. A. Bobb, G. Zhu, M. Mayy, A. V. Gavrilenko, P. Mead, V. I. Gavrilenko, and M. A. Noginov, *Appl. Phys. Lett.* **95**, 151102 (2009).
- ⁵K.-P. Chen, V. P. Drachev, J. D. Borneman, A. V. Kildishev, and V. M. Shalaev, *Nano Lett.* **10**, 916 (2010).
- ⁶J. Rodriguez-Fernandez, A. M. Funston, J. Perez-Juste, R. A. Alvarez-Puebla, L. M. Liz-Marzan, and P. Mulvaney, *Phys. Chem. Chem. Phys.* **28**, 5909 (2009).
- ⁷D. M. Kolb, *Prog. Surf. Sci.* **51**, 109 (1996).
- ⁸L.-H. Shao, M. Ruther, S. Linden, S. Essig, K. Busch, J. Weissmüller, and M. Wegener, *Adv. Mater.* **22**, 5173 (2010).
- ⁹M. Smetanin, R. N. Viswanath, D. Kramer, D. Beckmann, T. Koch, L. A. Kibler, D. M. Kolb, and J. Weissmüller, *Langmuir* **24**, 8561 (2008).
- ¹⁰M. H. Hölzle, V. Zwing, and D. M. Kolb, *Electrochim. Acta* **40**, 1237 (1995).
- ¹¹M. A. Schneeweiss and D. M. Kolb, *Solid State Ionics* **94**, 171 (1997).
- ¹²G. Lippmann, *Ann. Chim. Phys.* **5**, 494 (1875).
- ¹³C. M. Soukoulis, S. Linden, and M. Wegener, *Science* **315**, 47 (2007).