Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 171 (2017) 139–143

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Etchant-based design of gold tip apexes for plasmon-enhanced Raman spectromicroscopy

Sergey Kharintsev [a,b,*], Alexander Alekseev [c,d], Joachim Loos [e]

[a] Department of Optics and Nanophotonics, Institute of Physics, Kazan Federal University, Kremlevskaya, 16, Kazan 420008, Russia
[b] Tatarstan Academy of Sciences, Baumana str., 20, Kazan 420111, Russia
[c] National Laboratory Astana, Nazarbayev University, Kabanbay batyr ave., 53, Astana 01000, Kazakhstan
[d] STC NMST, Moscow Institute for Electronic Technology, Moscow, Russia
[e] DSM Resolve, 6167 RD Geleen, The Netherlands

ARTICLE INFO

Article history:
Received 22 March 2016
Received in revised form 22 July 2016
Accepted 31 July 2016
Available online 2 August 2016

Keywords:
Optical antenna
Gold tip
Tip-enhanced Raman scattering
Optical near-field
Surface plasmon
Electrochemical etching
Polyimide
Polyethelene
Enhanced optical spectroscopy
Calibration grating
Etchant effect

ABSTRACT

In this paper, we gain insight into the design and optimization of plasmonic (metallic) tips prepared with dc-pulsed voltage electrochemical etching gold wires, provided that, a duty cycle is self-tuned. Physically, it means that etching electrolyte attacks the gold wire equally for all pulse lengths, regardless of its surface shape. Etchant effect on the reproducibility of a curvature radius of the tip apex is demonstrated. It means that the gold conical tips can be designed chemically with a choice of proper etchant electrolyte. It is suggested to use a microtomed binary polymer blend consisting of polyamide and low density polyethylene, as a calibration grating, for optimizing and standardizing tip-enhanced Raman scattering performance.

1. Introduction

Optical spectroscopy based on tip-enhanced Raman scattering (TERS) has paved a new way to visualize and chemically characterize single molecules, quantum dots, thin films and other nano-patterned materials with nanometer spatial resolution [1–3]. Initially, it has become possible due to combination of Raman spectroscopy and scanning probe microscopy [4–6] – an emerging nanoscale chemical mapping method. Here, a major challenge is to couple laser light and a tip apex of an AFM cantilever or an optical antenna, in which highly localized surface plasmons (LSP) are excited. For this purpose, the optical antenna material should necessarily be plasmonic. The highest enhancement factors have been achieved with bulk plasmonic materials (gold and silver in the visible region) [7]. Therefore, the design of optical antennas and optimization of their parameters such as curvature radius, aspect ratio etc., play a crucial role in enhanced optical spectromicroscopy. Accessing to non-propagating (confined) optical fields, the antenna empowers us to go beyond the Abbe's diffraction limit and capture diffraction-free optical images of a sample under study. Being within the mainstream, the optical antennas are widely used as plasmonic biosensors [8], waveguides [9] and meta-material constituents [10].

Basically, the bulk metallic antennas are fabricated with electrochemical etching [1,11–13] and focused ion beam milling [14]. With the methods, considerable progress has been achieved for shaping mesoscopic surfaces of the optical antennas [15], whereas the reproducibility and reliability of well-defined tip apexes remain ambiguous [16]. In this context, under design of the optical antennas, the morphology of their mesoscopic surface is commonly understood; in particular, one deals with nanoparticles, nanorods, conical tips, self-similar antennas, bow-tie gap antennas, tip-on-aperture antennas and others [17–23]. Creation of the tip apex acting as a hot spot for effectively coupling/decoupling optical near- and far-fields is a task of high priority. One should distinguish the reproducibility of an antenna's mesoscopic structure from that of its tip apex and, therefore, we can introduce a concept for *controlled design* of the tip apexes, in our case, by tuning their curvature radii. It means that the reproducibility of the tip apex with the given parameters plays a more important role compared to fabricating apical tips with curvature radii as small as possible. Imperfect geometry

* Corresponding author at: Department of Optics and Nanophotonics, Institute of Physics, Kazan Federal University, Kremlevskaya, 16, Kazan 420008, Russia.
E-mail address: skharint@gmail.com (S. Kharintsev).

http://dx.doi.org/10.1016/j.saa.2016.07.048
1386-1425/