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A dedicated multilayer technique for the fabrication of three-dimensional metallic nanoparticles

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ABSTRACT

High resolution electron-beam lithography has been applied to the fabrication of three-dimensional metallic nanostructures. The herein developed fabrication process, which is demonstrated at the example of two ensembles of complex nanoscale particles, comprises a dedicated combination of multilayer electron-beam exposure, vacuum evaporation, lift-off and dry etching. The designs of the two nanostructures rely on the principles of a low degree of spatial symmetry and a high degree of chirality, respectively. Their optical properties are evaluated by means of far-field transmittance spectroscopy. Our fabrication technique delivers an excellent quality of miniaturized three-dimensional nanostructures and yields great potential to be extended towards the fabrication of large-area optical metamaterials composed of truly three-dimensional metallic nanoparticles.

1. Introduction

During the past decades metallic nanoparticles have been subject to intense research pursuing their fascinating interaction with light. Particularly, the realization of deliberately designed nanomaterials has led to the advent of optical metamaterials [1], a novel material class which supplements the optical functionalities provided by natural materials in many intriguing ways. However, from the point of view of nanofabrication, most metallic nanoparticles are fabricated by top-down approaches as a single functional layer only, limiting the control of the structural variation in the third spatial dimension [2]. This constraint manifests their quasi two-dimensional character, considerably restricting mirror and rotational symmetry properties and thus the degrees of freedom in nanoparticle design. Most notably, in many cases the interaction between light and matter necessitates three-dimensional structures. Circularly polarized light, for instance, is inherently connected to chiral structures, which are three-dimensional by definition [3]. While the majority of recent studies addressed this issue by the subsequent stacking of several functional layers fabricated by top-down approaches [4–6], truly single-block metallic nanoparticles are notable exceptions and have been limited to feature sizes on the micrometer scale [7,8]. Complementary approaches often utilize chemically or thermally driven self-assembly to obtain truly three-dimensional micro- and nanostructures [9,10], but the freedoms of design in such bottom-up approaches are considerably restricted when compared to elaborated pattern composition regimes like electron-beam lithography (EBL). Last but not least, the application of direct laser writing in combination with a stimulated emission depletion technique is currently evaluated as an alternative approach for the down-scaling of truly three-dimensional nanostructures [11], provided that early hopes on spatial resolution improvements can be substantiated [12].

In this contribution we address the further miniaturization of three-dimensional metallic nanoparticles for optical metamaterials by an EBL based multilayer technique. Starting from a standardized process for stacked nanostructured layers [13], we advance the state-of-the-art technological capabilities by describing how genuine three-dimensional, periodically arranged, metallic nanoparticles can be fabricated by a dedicated technique combining lift-off techniques and selective dry etching. This is a substantial advancement, given that the majority of related nanostructures consist of a small number of stacked planar layers and does not provide a substantial structural variation in the third spatial dimension. We show how this approach allows for three-dimensional chiral nanostructures which enabled the first experimental proof of a novel optical effect, namely the asymmetric transmission of linearly polarized light, and the demonstration of a giant optical activity, for which the three-dimensional character of the associated nanoparticles was an essential prerequisite. Our results are substantiated by polarization-resolved optical spectroscopy of the fabricated samples.

2. Three-dimensional nanostructure designs

In the following we describe two distinct nanoparticle geometries which are feasible by the herein proposed method. The first

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particle follows the design guidelines of a low-symmetry nanostructure that is intended to show asymmetric transmission of linearly polarized light [14]. To meet the requirements as described in [14], a simple geometry that consists of two metallic elements was designed. The ensemble they constitute is essentially three-dimensional, anisotropic, and chiral. The geometry of this two-element nanostructure contains two closely spaced layers and is shown in Fig. 1a and b. It. The bottom layer comprises an L-shaped metallic particle and the top layer a single nanowire. This combination breaks the symmetry of the overall arrangement and leads to a genuine three-dimensional chiral nanoparticle. It is noteworthy that such anisotropic and low-symmetry nanoscale arrangements can hardly be fabricated by chemical synthesis approaches, because thermodynamic equilibrium conditions will rather favor symmetric particles without substantial control of their mutual orientations and arrangement [15]. By contrast, a multilayer EBL technology enables both to control the pattern of each single layer independently and to provide a precise lateral and vertical arrangement of the structures, for instance on a well defined periodic grid.

The second design we considered is the so-called loop-wire particle, whose plasmonic and optical properties are described in detail elsewhere [16,17]. This structure consists of a cut-wire split-ring resonator combination. The loop-wire particle as seen from two different perspectives is schematically depicted in Fig. 1c and d. We stress that a pronounced structural variation of the particle in the third dimension is essential for its optical performance. This particular requirement cannot be met by a simple stacking of subsequent layers [4], but calls for an adapted combination of etching and deposition techniques.

Both nanoparticle designs described above should be completely embedded in an index-matched dielectric host to rule out asymmetric effects due to the presence of the indispensible substrate [18]. Furthermore, it is convenient to assemble a large number of these elements onto a periodic grid in order to facilitate their optical far-field characterization [19,20].

3. Nanofabrication technique

To fabricate the described metallic nanostructures, the stacking of a distinct number of lithographic patterns was applied. The first layer was equipped with additional alignment marks to allow for a precise lateral alignment of subsequent EBL steps. The starting point was a 4 in. diameter fused silica wafer which was 1 mm thick and polished on both sides. For the EBL an 85 nm thick layer of the polymethyl methacrylate (PMMA) copolymer AR-P610 from Allresist Berlin GmbH was prepared by spin coating and tempered at 210 °C for 10 min. Subsequently, the resist AR-P 671 from the same supplier was spin coated with the same thickness and baked at 180 °C for 30 min. This preparation resulted in two PMMA layers with two different electron selectivities in order to provide an undercut resist profile for the purpose of lift-off. Next, a 10 nm thick gold layer was thermally evaporated to ensure a conducting surface for EBL. During electron beam exposure with a variable-shaped beam electron-beam writer Vistec SB350 OS [21], typical electron exposure doses were of the order of 400 $\mu C/cm^2$. After the wet chemical removal of the gold conductance layer in an aqueous solution of potassium and potassium iodide, the samples were developed in a 1:1 methyl isobutyl ketone (MIBK):isopropanol solution for 30 s, rinsed with isopropanol and blown dry by nitrogen. After exposure and development, an adhesion promoting titanium film with a thickness of 3 nm and a gold layer with a thickness of 50 nm were deposited onto the resist patterned wafer by physical vapor deposition. The deposition rates were chosen to be smaller than 1 Å/s aiming at a superior optical quality compared to higher rates [22]. Subsequently the wafer was immersed in acetone for more than 4 h and finally a lift-off supported by sonication was performed. After that, the layer was planarized by hydrogen silsesquioxane (HSQ; xR-1541:MIBK 1:1 from Dow Corning) by adapting a process optimized for obtaining superpolished surfaces for extreme ultraviolet light applications [23]. The HSQ solution was spin coated such that a 120 nm thick film would have been obtained on a planar substrate. Then the samples were baked for 2 min at 120 °C and for 5 min at 170 °C on a hot plate to remove residual solvents. A curing step was performed with ultraviolet light for 1 h. The benefit of HSQ is that the finished coating is mechanically stable and optically nearly equivalent to the silica substrate underneath. The effect of planarization was confirmed with atomic force microscopy (AFM). In case of the low-symmetry nanoparticles shown in Fig. 1(a) and (b), this bottom layer process was repeated for the top layer, where simple nanowires were lifted in gold. Local milling of the finished nanostructures at two different depths with a focused ion beam verified the lateral alignment accuracy to be better than 20 nm (Fig. 2(a)).

The fabrication process of the loop-wire nanoparticle relied on the same process concerning the bottom layer and combined three times EBL, two times metal lift-off and numerous dry etching steps. The whole process chain is schematically displayed in Fig. 3. Basically, two metallic nanoparticles (called L-structures in the following) with two orthogonally oriented arms of different lengths were placed on top of each other and separated by a dielectric spacer. They were arranged such that the two long arms are parallel aligned and the two short arms were directed in opposite directions. The two long arms were connected at their extremities, thus forming a loop-wire nanostructure altogether. After the planarization of the bottom layer with L-shaped gold nanostructures (Fig. 3a and b) and their respective planarization as described above, this layer was thinned with CF_4-based reactive ion beam etching (RIBE; with a home made etching tool with a 150 mm ion source of Kaufmann-type) until a distance of 110 nm from the plane of the substrate was reached. At this stage, a quasi-planar surface covering the L-structures was obtained (Fig. 3c). After depositions of 20 nm chromium and 200 nm FEP171 resist from Fujifilm Arch, a second EBL-step was performed to define a groove perpendicular to the long arm of the L-shaped nanoparticles. This groove was

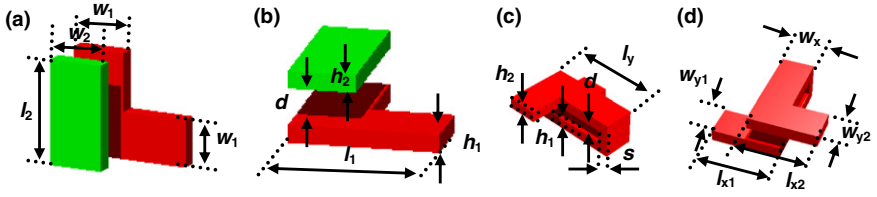

Fig. 1. (a and b) Two sketches of the two-element low-symmetry nanostructure from two different perspectives along with the definition of all geometrical parameters: $l_1 = l_2 = 290$ nm, $w_1 = w_2 = 130$ nm, $h_1 = h_2 = 40$ nm, $d = 80$ nm. (c and d) Two sketches of the loop-wire nanoparticle from two different perspectives along with the definition of all geometrical parameters: $lx_1 = 280$ nm, $lx_2 = 290$ nm, $l_y = 420$ nm, $w_x = wy_1 = wy_2 = 155$ nm, $h_1 = h_2 = 50$ nm, $d = 60$ nm, $s = 50$ nm.