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Tuning the plasmonic behavior of metallic nanowires

Robert Krajcar [a,*], Richard Denk [b], Peter Zeppenfeld [b], Petr Slepička [a], Václav Švorčík [a]

[a] Department of Solid State Engineering, University of Chemistry and Technology, 166 28 Prague, Czech Republic
[b] Institute of Experimental Physics, Johannes Kepler University, A-4040 Linz, Austria

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ABSTRACT

The Localized Surface Plasmon Resonance (LSPR) of metallic nanowire arrays was studied as a function of wire thickness and composition. Ripple-like periodic structures on polymer foils were produced using an excimer laser. Nanowire arrays were prepared on these nano-patterned polymer surfaces via vacuum evaporation of silver and gold at grazing angle of incidence. Different widths of the wires were obtained by a second grazing incidence evaporation process on the still uncoated side of the polymer ridges. Using different metals for each deposition step, mixed nanowires were prepared. The sample geometry was analyzed by FIB–SEM. The optical properties of the nanowires were studied by polarization resolved optical transmission spectroscopy revealing systematic shifts of the plasmon peak with respect to composition and width of the wires.

1. Introduction

Recently, great attention has been devoted to Localized Surface Plasmon Resonances (LSPRs) of metal nanoparticles [1]. These excitations, confined within the small volume of a particle, have non-propagating character. As a consequence, localized plasmon modes can be excited naturally by light. Inside vanishingly small spherical nanoparticles the phase of the oscillating field is practically constant, so a dipole moment is induced inside the particle. The associated polarizability experiences a maximum under the Fröhlich condition:

$$Re[\varepsilon(\omega)] = -2\varepsilon_m, \quad (1)$$

where $Re[\varepsilon(\omega)]$ is the real part of dielectric function of the metallic nanoparticle and ε_m is the dielectric constant of the surrounding medium [2]. The associated optical response is called a dipolar surface plasmon resonance, and its dependence on ε_m can be exploited for the construction of sensing devices [3]. This resonance in polarizability also implies field-enhancement effects, which are widely used in Surface Enhanced Raman Scattering (SERS) [4]. Typically, nanoparticles are supported on a dielectric substrate, whose permittivity also alters the optical properties of such a system [5]. Elongated nanoparticles exhibit a splitting of the plasmon resonance, due to different resonance frequencies for oscillations along the major and minor axes, respectively. The spectral positions of the plasmon resonances then depend strongly on the aspect ratio of the particle [6]. When the dimension of the major axis in rod- or wire-like structures exceeds the wavelength of the incident light, only oscillations along the minor axis can be excited by light. The excitation of the plasmon thus depends on the direction of polarization of the incident electromagnetic wave.

Size and shape, environment and chemical composition thus determine the optical response of nanoparticles, offering the possibility to create structures with desired optical properties. Noble metals are of a particular interest at the nanoscale: silver for its conductivity and antibacterial properties [7] and gold for its chemical stability. Both materials can be used to fabricate nanostructures whose localized plasmon resonances lie within the visible spectral range.

This work deals with the preparation and characterization of various types of metallic nanowire arrays fabricated by vacuum evaporation of Au and Ag on nano-patterned polyethyleneterephthalate foils. Laser stimulated fabrication of periodically patterned polymer surfaces [8] and the subsequent preparation of metallic nanowires have been investigated earlier by our group [9–11]. Here we focus on the plasmonic behavior of such structures with respect to wire width and composition. The aim of this work is to prepare a photosensitive layer, which responds to photons of a defined energy and polarization state. Therefore, great emphasis is also laid on sample characterization from a morphological and chemical point of view. Finding the relation between structure and optical properties will allow to adapt of the

* Corresponding author.
E-mail address: krajcarr@vscht.cz (R. Krajcar).

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manufacturing process to a given application.

2. Experimental

2.1. Materials, apparatus and procedures

As template for nanowire growth, a periodically patterned, rippled surface was produced by irradiating biaxially oriented polyethyleneterephthalate (PET) foils (Goodfellow Ltd., thickness 50 μm) with a KrF excimer laser (COMPexPro 50F, Coherent, Inc., wavelength 248 nm, pulse duration 20–40 ns, repetition rate 10 Hz) (Fig. 1A and B). The laser light was linearly polarized by means of a UV-grade fused silica prism (model PBSO-248-100). The modification was accomplished with 6000 laser pulses and a fluence of 7 mJ cm^{-2}. The angle of incidence was either 0° or 45°

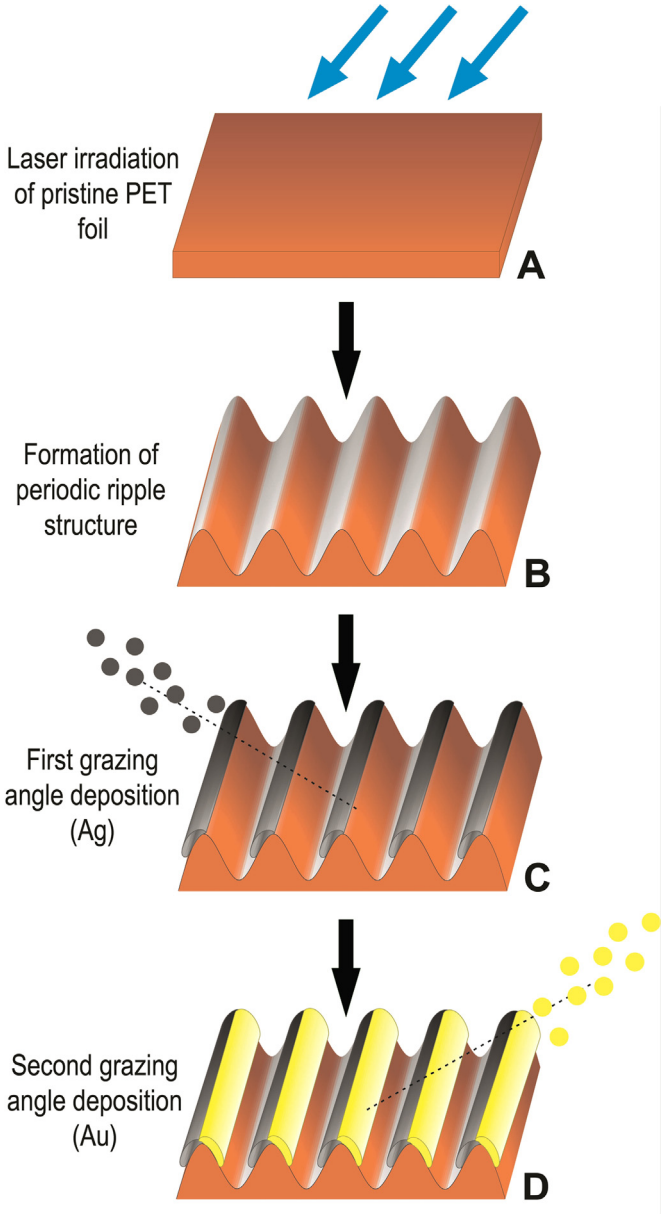

Fig. 1. Schematic illustrating the preparation of a Ag/Au_20/20 sample: (A) laser irradiation of the pristine PET foil leads to (B) formation of a periodic ripple structure. (C) Single-sided nanowires are fabricated by a first deposition at grazing angle of incidence, and (D) double-sided or mixed nanowires are obtained by a subsequent second deposition.

(with respect to the surface normal) resulting in a periodicity of the ripple pattern of $\Lambda = 230$ nm or $\Lambda = 427$ nm, respectively.

The irradiated PET foils were used as substrates for the subsequent deposition of silver (SAFINA, purity 99.99%) and gold (SAFINA, purity 99.99%) by vacuum evaporation (LEYBOLD-Heraeus, Univex 450 device, room temperature, pressure of 3.10^{-4} Pa). A direct assessment of the thickness of the deposited metal films was accomplished by scratch tests on glass substrates, which were coated simultaneously with the PET templates, using atomic force microscopy (AFM) in contact mode.

Nanowire arrays are obtained by deposition at 70° grazing angle of incidence (see Fig. 1C). This geometry allows to grow wires partially on one side and on the top of the polymer ridges. Rotating the sample after the first deposition by 180° and performing a second deposition then results in nanowires covering both sides of the ridges (see Fig. 1D). For convenience we will refer to nanowires created by a single deposition as “single-sided” nanowires, those fabricated by two depositions as either “double-sided” or “mixed” nanowires, depending on whether the same or different metals were used for both depositions, respectively. Single-sided nanowires are specified by *A_X* and double-sided or mixed nanowires by *A/B_X/Y*. Here *A* and *B* denote the metals of first and second deposition, respectively, while *X* and *Y* are the respective film thicknesses in nm. For instance, Ag/Au_40/15 refers to a mixed nanowire, where 40 nm of Ag has been deposited first, followed by a second deposition of 15 nm of Au from the opposite direction.

2.2. Analytical methods

The optical properties of the nanowire arrays were studied by Variable Angle Spectroscopic Ellipsometry (VASE, J. A. Woollam XLS-100), where the cross-polarized transmission mode was used to determine the polarization depended transmission at normal incidence.

Focused Ion Beam Scanning Electron Microscopy (FIB–SEM, LYRA3 GMU, Tescan, CR) was used for morphological characterization of the samples. Incisions were made with a gallium ion beam. A polishing procedure was applied to clean and flatten the investigated surfaces. The images were recorded under an angle of incidence of the electron beam of 54.8°. Using the same instrument, also chemical analysis of the samples was performed via Energy Dispersive Spectroscopy (EDS) measurements under normal incidence.

3. Results and discussion

SEM microscopy images, as shown in Fig. 2, reveal the exact location of the metal on the polymer ridges for single (Fig. 2A) and mixed nanowire arrays (Fig. 2B) grown on templates with a periodicity of 427 nm. As intended, for single-sided nanowires the metal crystallizes on the top and at one side of the ripples, which is caused by the deposition at a grazing angle of 70°. After a second deposition, almost the entire area of the ripples is covered by metal (Fig. 2B), but the wires are still well separated.

The chemical composition of a mixed nanowire array (Ag/Au_20/20, $\Lambda = 427$ nm) as studied with EDS is presented in Fig. 3. Fig. 3A shows an SEM image of the analyzed area. An EDS line scan (Fig. 3B) was performed across three nanowires. The line scan describes the local elemental distribution of the silver/gold nanowires in terms of detector counts characteristic of the respective metal. As expected, the gold signal (red line) is shifted laterally with respect to the silver signal (green line). On top of the ripples both signals overlap and a stronger signal is obtained from gold, as it was deposited after the silver.